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Chemically Induced Radio-frequency Emission and Chemical Radiophysics

A.L.Buchachenko and V.L.Berdinskii

Chemical reactions involving free radicals can yield molecules with inverted populations of the nuclear Zeeman levels and able to store energy in the nuclear Zeeman reservoir. These molecules produce a radio-frequency electromagnetic field which induces radiative transitions between the Zeeman levels resulting in the conversion of the stored energy into radio-frequency emission from the molecules. The dependence of the recombination probability of the radicals on their spin state allows the elementary acts of radical reactions to be controlled by the application of radio-frequency electromagnetic fields ("chemical" radio receiver). The generation and reception of r.f. radiation in chemical reactions are the object of a new field of science: chemical radiophysics. 29 references.

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I. INTRODUCTION

Chemical reactions are used to produce either new substances and materials or energy. The chemical energy released during a reaction "heats up" the translational, vibrational, and rotational motion of the molecules, and excites their electron shells. The emission of heat and light by the reacting system is a result of this "pumping" of energy into the molecules. More "organised" methods of converting chemical energy into radiation (chemical lasers) have been studied in recent years, and the mechanisms of the chemical action of laser radiation have been determined[1]. In the whole of that work the energy of the chemical reactions was emitted in the visible or infrared region of the spectrum.

We have recently observed emission at radio frequencies[2] from chemical reactions, resulting from the energy pumping of the Zeeman nuclear levels which act as an energy reservoir for the molecule. This new phenomenon (chemically induced radio-frequency emission) offers a bridge between the previously unrelated sciences of chemistry and radiophysics.

The aim of this review is to examine the physicochemical foundations and the theory of this new phenomenon, to establish the present state of knowledge on the effect of radio-frequency fields on the elementary acts of chemical reactions in solids, liquids, and gases, and to discuss the chemical consequences and the prospects of new developments in physical chemistry arising from this phenomenon. Problems of fundamental importance in chemical radiophysics

include: firstly, the role of the spin degrees of freedom of the molecules and radicals in chemical reactions, and the mechanism of the chemical pumping of the nuclear Zeeman levels; secondly, the way and the conditions under which the energy stored in the Zeeman reservoir is converted into the energy of radio-frequency emission; thirdly, the conditions and the mechanism which enable a radio-frequency field, acting on the spins of electrons and nuclei, to influence the chemical behaviour of atoms, molecules, and radicals.

II. CHEMICAL PUMPING

Transitions between nuclear Zeeman levels are accompanied by reorientation of the nuclear spins and magnetic moments which interact with the external magnetic field. Hence the pumping of the Zeeman reservoir (i.e. the creation of an excess or even an inverted population of the upper Zeeman levels) is equivalent to creating a negative polarisation of the nuclei. The mechanisms of chemically induced nuclear polarisation are well known[3-5], and the phenomenon of chemical polarisation of the nuclei (CPN) was discovered[6,7] in 1967. It was found that in chemical reactions involving paramagnetic particles (free radicals) a non-equilibrium population of the nuclear Zeeman levels is developed in the product molecules, resulting in nuclear polarisation (positive if the excess population resides in the lower Zeeman level, and negative if the population excess, or even inversion, affects the upper level). The non-equilibrium occupancy of the levels manifests itself in the nuclear magnetic resonance spectra of the product molecules as an anomalously strong absorption (for positive CPN) or induced emission (for negative CPN). Some examples of CPN are shown in Fig.1.

Chemical polarisation of the nuclei is created during the elementary acts of the interaction between radicals: their recombination, or their disproportionation. It arises from spin-forbidden processes in chemical reactions. The simplest physical interpretation of this phenomenon is the following. Spin (i.e. the momentum of rotation of the electrons and nuclei) is conserved in chemical reactions, and therefore reactions involving a change of spin are rigidly forbidden. Thus when two radicals collide their electronic spins can either be added (total spin of the pair $S = 1$, triplet state) or subtracted ($S = 0$, singlet state). The products of the recombination of radicals are usually diamagnetic, i.e. they have zero spin, and therefore they must have been formed from singlet radical pairs. Triplet pairs do not recombine. However, triplet–singlet conversion of the pair can take place during the lifetime of the triplet pair under the influence of the external magnetic field and of the internal (hyperfine, or Fermi) interaction between electrons and nuclei. The rate of conversion depends on the orientation of the spins and of the magnetic moments of the nuclei: for some orientations the rate is high, and radical pairs having these orientations are rapidly converted into the singlet state and recombine, giving reaction products.

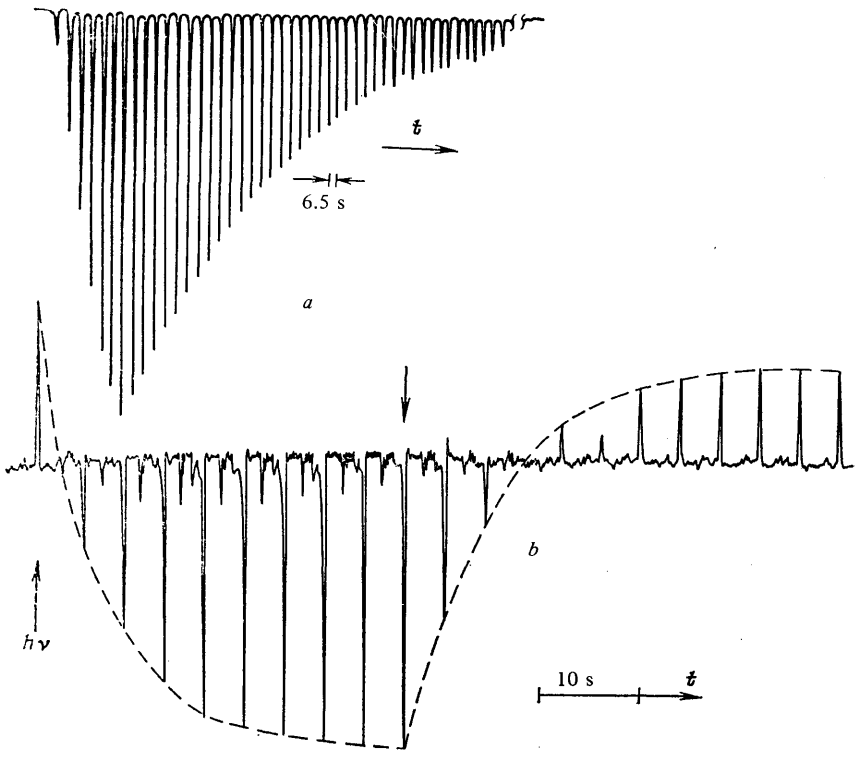


Figure 1. Chemical polarisation of ^{31}P nuclei in trimethylphosphate during the reaction with cyclohexylperoxydicarbonate (*a*), and of the protons in the CH_2 groups of dibenzylketone during photolysis (*b*). The arrows denote the switching on and off of the light.

In the radical pairs with the opposite nuclear orientation the triplet–singlet evolution is hindered, and the radicals in these pairs give different products. In this way the chemical reaction can "sort" the radicals for nuclear spin orientation and direct the radicals with a given type of nuclear orientation towards certain products and those with the opposite type towards other products. In this way some reaction products acquire a positive nuclear polarisation while others acquire a negative polarisation. As a rule, because of differences in chemical shift, the nuclei in the various products are characterised by different NMR frequencies, and therefore CPN is easily detected by NMR.

The sign of the CPN depends on the initial spin state of the radical pair, on the difference between the g-factors of the radicals, and on the sign of the hyperfine electron–nucleus interaction, but the CPN is invariably of opposite signs in the products of radical recombination and in the products of other radical conversions (without recombination). Obviously, the sign of the CPN is determined by the chemical nature of the radicals and by the type of chemical reaction involving the radical pair.

The sorting of nuclei with respect to orientation as a CPN mechanism is characteristic of reactions taking place in strong magnetic fields (about 10^3 Oe).[3] In weak magnetic fields (including the Earth's field) the reaction orients the nuclei as well as sorting the nuclei according to orientation. The electron–nucleus magnetic interaction couples the electrons and the nuclei into a single system in which the total angular momentum (spin) is conserved, so that the change in spin of one particle (electron) can be compensated by the change in spin of another (nucleus). Therefore the triplet–singlet conversion of the radical pair is accompanied by nuclear polarisation: the nuclei are transferred from the lower to the upper Zeeman level and are oriented against the field, producing an excess population of the upper level and a negative polarisation. In this mechanism of CPN the sign of the nuclear polarisation is again dependent on the initial spin state of the radical pair.

Thus the chemical interaction of radicals, being selective with respect to the electron spin of the radical pair, is also selective with respect to nuclear spin, since the two spin systems (electrons and nuclei) are coupled through the magnetic hyperfine interaction.

In principle, any nucleus having a non-zero magnetic moment can be polarised during the reaction, but CPN is most often observed in the widely distributed isotopes with a nuclear spin of $I = 1/2$, such as ^{1}H, ^{13}C, ^{19}F, ^{31}P, ^{119}Sn, etc.

Since radical recombination takes place in all radical reactions, CPN may be found in practically all reactions involving a free-radical step, and it may be treated as unambiguous proof of the existence of such a step. Therefore CPN has become an important method of establishing the mechanism of chemical reactions, and is now widely used for this purpose.

The magnitude of the CPN is measured by the polarisation coefficient P. Under Boltzmann equilibrium conditions the populations of the upper and the lower Zeeman level are n_-^0 and n_+^0 respectively, and under non-equilibrium conditions (i.e. in the presence of polarisation) the quantity P is defined by the expression

$$P = \frac{n_+ - n_-}{n_+^0 - n_-^0} , \qquad (1)$$

where n_+ and n_- are the non-equilibrium occupancies of the lower and the upper level. The polarisation coefficient is a measure of the factor by which the non-equilibrium occupancy difference created in the molecules at the instant of their generation from the radical pair exceeds the equilibrium value. With positive polarisation $n_+ > n_-$ and $P > 0$, whereas with negative polarisation we have a population inversion of the Zeeman levels and $P < 0$.

The quantity P depends on the spin and magnetic moment of the nucleus, on the electron–nucleus interaction energy, on the difference between the g-factors of the radicals in the pair, and on the strength of the magnetic field, i.e. on all the magnetic parameters which determine the rate of the triplet–singlet transitions of the radical pairs (spin dynamics). Furthermore P also depends on the diffusional mobility of the radicals (the molecular dynamics of the pair) and on the lifetime of the radicals (chemical dynamics), which jointly determine the time during which the pair must exist in order to undergo triplet–singlet conversion. Knowing the parameters of the spin, the molecular, and the chemical dynamics of the radical pair we can calculate the parameter P (see Refs.3 and 4 for a more detailed discussion).

The energy stored in the Zeeman reservoir as a result of nuclear polarisation is easily calculated. The ratio of the equilibrium occupancies is

$$n_+^0/n_-^0 = \exp(\hbar\gamma_n H_0/2kT) \approx 1 + \hbar\gamma_n H_0/2kT , \qquad (2)$$

where $\hbar\gamma_n H_0$ is the energy of the radio-frequency quantum, i.e. the excess energy of the nucleus in the upper Zeeman level (γ_n is the gyromagnetic ratio of the nucleus, and H_0 is the magnetic field intensity), and kT is the thermal energy. From this expression we obtain the Zeeman energy of N polarised nuclei in a magnetic field H_0:

$$E_z = -\frac{1}{2} PN(\hbar\gamma_n H_0)(\hbar\gamma_n H_0/2kT) , \qquad (3)$$

For example, in a field of 15000 Oe the Zeeman energy of 1 mole of protons with a polarisation coefficient $P = -10^3$ is $\sim 10^{-4}$ J at 30 °C. The energy of the Zeeman reservoir is proportional to the nuclear polarisation coefficient, and therefore the chemically induced emission of radio frequencies is most likely to be found in reactions with strong nuclear polarisation.

The large absolute value of the polarisation coefficient $|P|$ is a striking feature of CPN: values of 10^2–10^4 are common. However, in some reactions the coefficient $|P|$ can be even larger and approach the limiting value $P_{\lim}$:

$$|P_{\lim}| = (2kT/\hbar\gamma_n H_0) . \qquad (4)$$

Thus in the photolysis of cyclododecanone in the liquid phase at 20 °C in a field of 125 Oe a coefficient $|P| > 3.6 \times 10^6$ was observed for the protons of this molecule, and the probability of transferring the proton to the upper Zeeman level by the absorption of one quantum of photochemically active light[8] was greater than 0.3, i.e. the quantum "yield" of the nuclear polarisation was ≥ 0.3.

In the photosensitised decomposition of cyclohexanone diperoxide in solution at 20 °C in a field of ~200 Oe, a coefficient $|P| > 4 \times 10^5$ was observed[9] in the resulting cyclohexane, with a quantum "yield" of ~0.036 for the nuclear polarisation. Though this value is an order of magnitude lower than in the previous case, it is surprisingly large, and well beyond the range accessible by using existing methods of orienting nuclei in the condensed phase (for example, the Oberhauser effect).

Thus chemical reactions can generate large amounts of nuclear polarisation and store large amounts of energy in the Zeeman reservoir of the reaction products.

III. SELF-EXCITATION OF CHEMICALLY INDUCED RADIO-FREQUENCY FIELDS

A population inversion of the Zeeman levels is a necessary but by no means sufficient condition for the emission of the Zeeman energy stored in the reaction products in the form of radiation. The frequencies of the transitions between the nuclear Zeeman levels depend on the strength of the external magnetic field and correspond broadly to the radio-frequency range (from super-long to ultra-short waves). In this range the probability of spontaneous radiative transitions between levels is very small. For example, for a proton in a magnetic field of 7500 Oe this probability is 10^{-25} s^{-1}, corresponding to an emission time of 10^{17} years[10]. This is enormously greater than the spin–lattice nuclear relaxation time (1–100 s), after which the occupancy of the Zeeman levels reverts to the equilibrium thermal (Boltzmann) distribution and the energy of the Zeeman reservoir is irreversibly converted into thermal energy of the lattice. Therefore it is important to establish the conditions under which the Zeeman energy of the reaction products is emitted as r.f. radiation instead of being converted into heat by the spin–lattice relaxation processes.

The magnetic moments of the negatively polarised nuclei (μ_n) can be combined into an overall magnetisation vector **M** oriented in opposition to the outer magnetic field. The reaction products will generate r.f. radiation, i.e. they will create the necessary electromagnetic field, only when self-excitation of the Larmor precession of the nuclear magnetisation vector **M** round the direction of the external field H_0 can take place (Fig.2). The antiparallel orientation of the vector **M** with respect to the field H_0 is unstable, and as a result of random fluctuations the vector **M** can deviate from this orientation and begin to rotate round the direction of the field H_0 (i.e. to precess). Once the precession has started the vector **M** begins to induce an electromagnetic field which forces it to deviate still further from the external field H_0 (Fig.2).

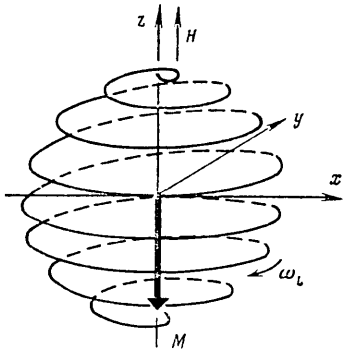


Figure 2. Precession of the magnetisation vector of negatively polarised nuclei. The tranverse components M_x and M_y are oscillating in the xy plane at the precession frequency ω_L.

The self-excitation of the precession of the vector **M** ensures the presence in the ensemble of molecules (reaction products) of transverse variable components of the total magnetisation $M_x(t)$ and $M_y(t)$, oscillating at the Larmor frequency $\omega_L = \gamma_n H_0$ in a plane perpendicular to the direction of H_0. The longitudinal component M_z varies slowly in chemical reactions. Therefore the radio-frequency electromagnetic field in the region surrounding the sample is generated only by the transverse component of the magnetisation, $M_\perp = (M_x^2 + M_y^2)^{1/2}$. If the sample containing chemically polarised reaction products is placed inside an induction coil the precessing vector **M** induces a high-frequency e.m.f. in the coil. This process is the exact analogue of the generation of an e.m.f. in the winding of any electrical generator, the only difference being that in this case the magnet is rotation (and not the rotor): the role of the rotating magnet is played by the transverse component of the nuclear magnetic moment. This is the simplest, classical account of the generation of a chemically induced radio-frequency field.

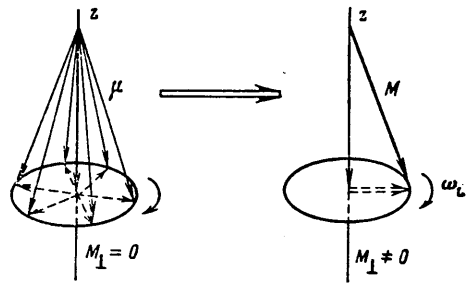


Figure 3. Transition from non-coherent motion to coherent precession of negatively polarised nuclear magnetic moments (frequency ω_L).

Self-excitation of the precession of the overall vector **M** denotes the appearance of spontaneous synchronisation (coherence) in the motion of the nuclear magnetic moments of the product molecules (Fig.3). In the absence of coherence the magnetic moments of the individual nuclei orientated against the field H_0 precess independently of each other, their precession phases are random, and the transverse components of the magnetisation are randomly "strewn" in the precession plane. As a result there is no net transverse magnetisation ($M_\perp = 0$). The r.f. electromagnetic field generated by the reaction acts on the magnetic moments of the nuclei and compels them to precess consistently, synchronously, and coherently, so that all the precessions are in phase, and the transverse components become aggregated in an overall vector $M_\perp \neq 0$. In other words the resulting coherent electromagnetic field induces a further avalanche-like increase in the synchronisation of the precession of the nuclear magnetic moments. The amplified electromagnetic field takes control of the precession of **M**, and as a result the (initially) negatively oriented magnetisation vector tends to become oriented along the field direction (Fig.2). This intrinsic coherent electromagnetic field induces forced radiative transitions between the Zeeman levels. The probability of forced transitions is very much greater than the probability of spontaneous emission, and therefore the energy of the Zeeman reservoir can be radiated instead of being dissipated as heat.

Thus the situation is similar, in principle, to that in a laser, where the emission of radiation is a forced (stimulated) process. It is therefore legitimate to treat the chemical reaction as a chemical quantum generator of radio frequencies: a raser (by analogy with the laser).

The coherence is perturbed by transverse magnetic relaxation processes through the random local fields H_{loc} which cause a scatter in the frequencies and phases of the precessing magnetic moments of the individual nuclei: the transverse components of the magnetisation vector become "dispersed", opposing the development of coherence (Fig.3). To ensure coherence, the field H^* created by the chemical reaction products, which "collects" the transverse components of the magnetisation, must be greater than H_{loc}: $H^* > H_{loc}$. In other words the coherence time T_2^* must be less than the nuclear transverse relaxation time T_2, i.e. the rate of development of coherence must be greater than the rate at which coherence is perturbed.

Thus two conditions must be fulfilled for the self-excitation of electromagnetic radiation in chemical reactions: negative polarisation of the nuclei, to allow energy to be stored in the Zeeman reservoir, and coherence of the nuclear spin system, to "rescue" the Zeeman energy from thermal relaxation and to stimulate its emission in the form of radiation. These two conditions are closely bound together: if the Zeeman energy is small, i.e. if the magnetisation vector M is small, the electromagnetic field induced by the precession of M and its coherence will both be weak, and they will be unable to compete with the transverse nuclear relaxation processes which perturb the coherence. Therefore in order to excite raser generation we need to achieve a well defined critical level of chemical nuclear polarisation (the vector M_z) corresponding to an amount of stored Zeeman energy called the generation threshold. A theoretical analysis of the self-excitation conditions and of the generation threshold is given in Section V.

IV. EXPERIMENTAL OBSERVATIONS OF RADIO-FREQUENCY GENERATION

Chemically induced radio-frequency emission was first observed in the photochemical reaction between porphyrin and quinone[2,11], and somewhat later in the thermal decomposition of benzoyl peroxide[12].

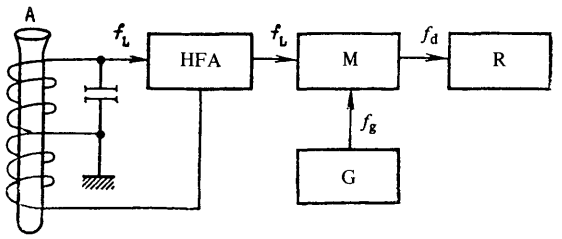


Figure 4. Block diagram of the radio circuit used to detect the chemically induced radio-frequency field: A is a tube containing the polarised reaction products, HFA is a high-frequency amplifier, M is a mixer, G is a standard generator, R is a recorder. The magnetic field H_0 is perpendicular to the coil axis[2].

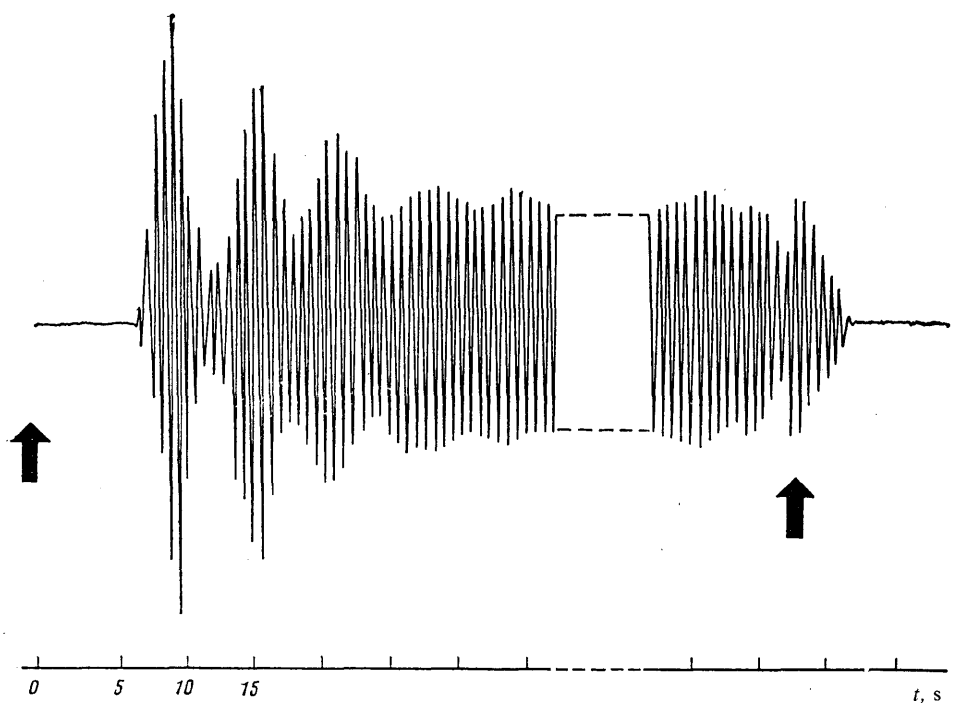


Figure 5. Chemically induced radio-frequency emission from polarised quinone molecules (signal recorded at the low frequency f_d; H_0 = const); the arrows denote the switching on and off of the light[2].

The reaction between porphyrin and *p*-benzoquinone is

$$\Pi \xrightarrow{h\nu} \Pi^*$$
$$\Pi^* + Q \xrightarrow{H^+} \Pi^{\dot{+}} + \dot{Q}H$$
$$\Pi^{\dot{+}} + \dot{Q}H \rightarrow \Pi + Q + H^+ ,$$

where Π is a porphyrin molecule (octamethyltetraphenylporphyrin), Q is the quinone, $\dot{Q}H$ is the semiquinone radical, and $\Pi^{\dot{+}}$ is the porphyrin cation radical. The ion radicals produced by the electron transfer reaction undergo disproportionation to give quinone molecules with negatively polarised protons. The result is a continuous pumping of

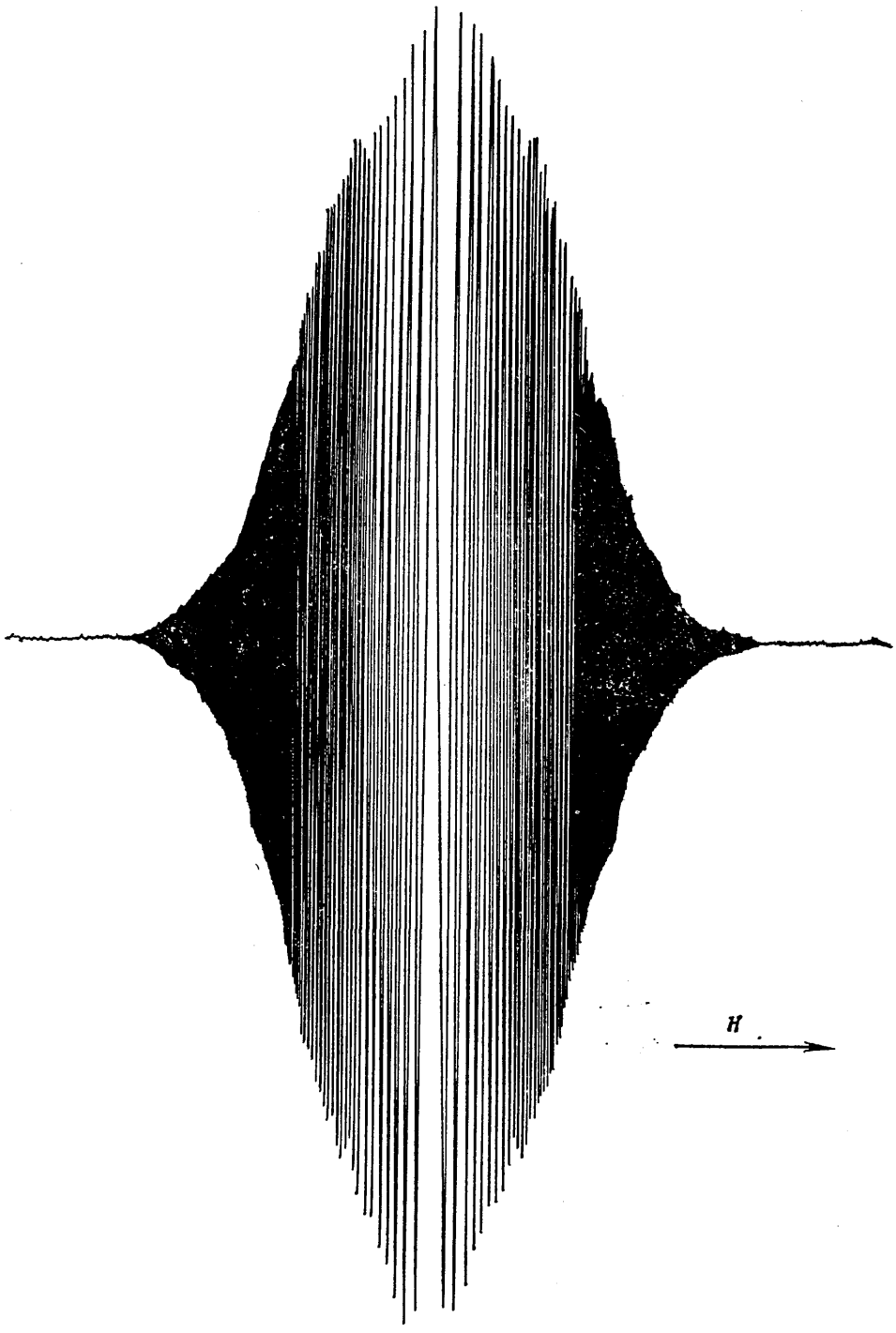


Figure 6. Chemically induced radio-frequency emission from polarised quinone molecules. Signal recorded with periodic variations in the field H_0.

the Zeeman energy reservoir of the protons in the quinone molecule, with a magnetisation vector oriented against the field H_0.

The reaction was carried out in a tube surrounded by the coil of an oscillator circuit, and initiated by light in the absorption band of the porphyrin (λ = 546 nm). The circuit was tuned to the frequency of the Larmor precession of the nuclear magnetisation vector of the quinone molecule (f_L = 100 MHz) in a field $H_0 \cong$ 24000 Oe, corresponding to an emission wavelength of 3 m. A block diagram of the radiation detection circuit is shown in Fig. 4. In order to lower the generation threshold the Q-factor of the oscillator circuit was increased by additional feedback from the high-frequency amplifier. After amplification of the signal from the chemically induced radio-frequency field a low-frequency signal is obtained at the difference frequency $f_d = f_L - f_g$ (where f_g is the frequency of the reference generator), and this is amplified by a low-frequency amplifier and displayed on a recorder and an oscilloscope. The self-excitation of the precession was additionally monitored at the high frequency f_L by an h.f. oscilloscope connected to the output of the high-frequency amplifier. A record of the chemically induced signal is shown in Fig. 5. Generation begins 5–10 s after the admission of light and the onset of the reaction, i.e. when the system reaches the generation threshold. After this short initial transient a steady-state regime is established: this regime can be maintained for a long time, because the reaction is almost ideally reversible. The radio-frequency generation stops when the light is switched off and the reaction comes to an end. The generation process can be repeated several times with the same sample by switching the photochemical pumping system on and off.

Fig. 6 shows a record of the radio-frequency generation obtained by slowly varying the field H_0 (by 10^{-3} Oe) with the recorder carriage connected to the field scan. Changes in field strength produce a change in the generation frequency f_L, and hence in the detected difference frequency f_d. Thus $f_d = 0$ at the centre of each bundle of signals, where the Larmor precession frequency coincides with that of the reference generator f_g, and f_d increases towards the edges of the bundle. This behaviour of f_d shows unequivocally that the signal is due to chemically induced radiation.

In another series of experiments[11] the radio-frequency field was detected in a crossed coil system (Fig. 7). The auxiliary coils are connected to the output of the high-frequency amplifier, and the generation signal is connected to the input of the same amplifier. As in the previous experiment, $H_0 \cong$ 24000 Oe, and the precession frequency is 100 MHz.

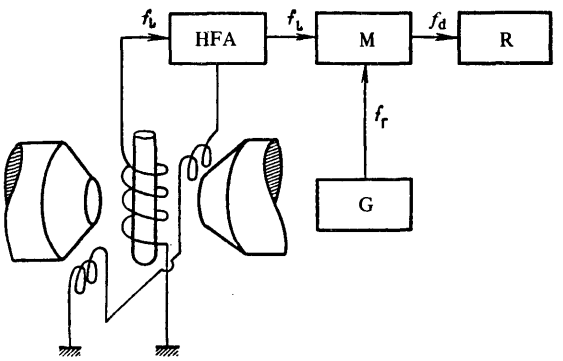


Figure 7. Block diagram of the apparatus used to detect the chemically induced radio-frequency field with crossed coils: HFA is a high-frequency amplifier, M is a mixer, G is a standard generator, R is a recorder[12].

The generation signals detected in this way from the photochemical reaction between porphyrin and quinone are shown in Fig. 8. The signals were recorded by amplitude detection with a constant field H_0. In this case steady-state generation is not established after the initial transient, and the emission consists of regularly spaced short bursts of radiation. In this regime the reaction system behaves like a radio-frequency "chemical pulsar".

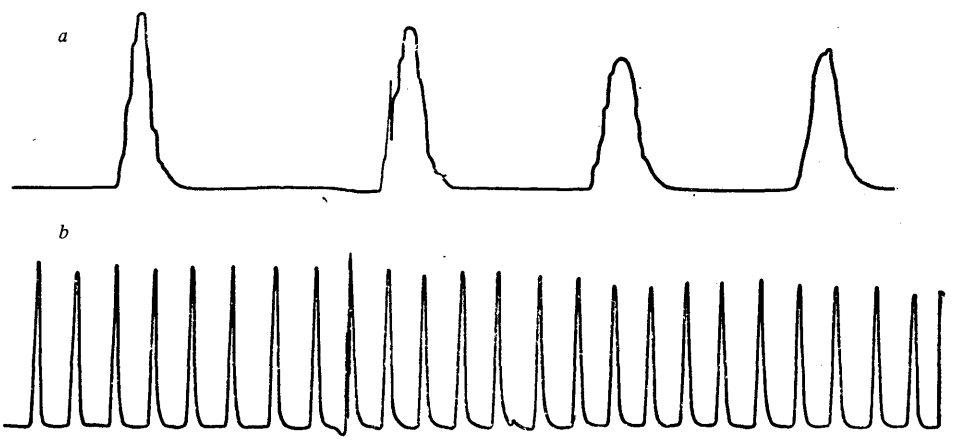


Figure 8. Chemically induced radio-frequency emission from quinone molecules in a constant field H_0 ("chemical pulsar" regime): *a*) duration of record 50 s, *b*) duration of record 250 s.[12]

The strength of the r.f. fields generated by the reaction products has been measured in experiments on the self-excitation of the precession of the total nuclear magnetisation vector **M** in a rotating system of coordinates[12], involving a non-resonant magnetic field H_1 rotating in a plane perpendicular to the constant field $\mathbf{H}_0$. The r.f. field was generated in the negatively polarised protons of the benzene molecules produced by the thermal decomposition of benzoyl peroxide in cyclohexanone (120 °C, peroxide concentration 0.5 M). The reaction involves free-radical steps, and is accompanied by strong negative polarisation of the benzene protons. From the CPN kinetics the effective rate constant of the reaction

$$(PhCO_2)_2 \xrightarrow{k} C_6H_6 \ ,$$

was determined ($k = 2 \times 10^{-2}$ s^{-1}), for which the polarisation coefficient is $P = -400$. Under these conditions the negative polarisation of the protons is retained for 3–4 min after the onset of the reaction. In these experiments the e.m.f. produced in the coil was measured: it was found to be ~2 μV, corresponding to a magnetic component of the electromagnetic field generated by the reaction of ~1.6×10^{-7} Oe. From this we can estimate the emission temperature as $T_{em} \cong 10^{28}$–10^{29} K, so that the energy of the non-equilibrium emission from the reaction is 25–27 orders higher than the energy of the equilibrium (Boltzmann) radio-frequency emission. In comparison we note that the energy of the radio-frequency radiation from one of the best known cosmic emitters (the OH radical maser) is only ~10^{13} K, i.e. the chemical radio-frequency generators are "brighter" than their cosmic analogues. However, the absolute efficiency of the chemical generator is negligibly small, because the heat capacity of the spin systems is low and only a very small fraction of the energy of the chemical reaction can be accomodated in the Zeeman reservoir.

V. THEORY OF THE CHEMICAL RASER

We have based a theoretical analysis[13] of the chemical radio-frequency generator on the standard Bloch equations which describe the behaviour of the nuclear magnetisation vector[14]:

$$\begin{aligned}
\frac{dM_x}{dt} &= \omega M_y - \gamma_n M_z H_y - 2\pi\Delta f M_x \\
\frac{dM_y}{dt} &= -\omega M_x + \gamma_n M_z H_x - 2\pi\Delta f M_y \\
\frac{dM_z}{dt} &= \gamma_n (M_x H_y - M_y H_x) - \frac{M_z - M_0}{T_1} + P\frac{dM_0}{dt} \ ,
\end{aligned} \qquad (5)$$

where M_x, M_y, and M_z are the components of the magnetisation vector, M_0 is the equilibrium magnetisation, H_x and H_y are the components of the variable magnetic field generated in the coil by the chemical reaction products, T_1 is the spin–lattice relaxation time of the nuclei, Δf is the half-width of the NMR line at half height, and γ_n is the gyromagnetic ratio for the nuclei of interest. Eqns.(5) differ from the conventional Bloch equations only in the term $P(dM_0/dt)$, which characterises the rate of generation of nuclear magnetisation by the reaction, i.e. the rate of chemical pumping.

The self-excitation threshold for the precession of the chemically induced nuclear magnetisation vector is defined by the condition

$$|M_z| > \Delta f/\gamma_n \eta q, \qquad (6)$$

where η is the filling coefficient of the coil and q is the Q-factor of the circuit. Of course, the parameter M_z should be negative. If the condition (6) is obeyed we expect self-excitation of the precession of the vector **M** (Fig.3). Under these conditions we observe a transverse component of the magnetisation, $M_\perp = (M_x^2 + M_y^2)^{1/2}$, whose value increases exponentially, and a high-frequency e.m.f. is induced in the coil. Its amplitude is given by

$$u = (4\pi/c)\, q w s \eta \omega_L M_\perp \ ,$$

where w is the number of turns in the coil, s is its cross-sectional area, and c is the velocity of light.

For unimolecular reactions of the type of A → B, with a rate constant k and polarisation coefficient P, the self-excitation condition becomes

$$\frac{(1 - PkT_1)^{1/(1-kT_1)}}{(1-P)^{kT_1/(1-kT_1)}} > 1 + \frac{\Delta f}{\gamma_n \eta q M_0} \ , \qquad (7)$$

where some of the quantities (P, k, M_0) are "chemical" parameters, others (Δf, η, T_1, q) are radiophysical.

The generation dynamics are illustrated in Fig.9: they were obtained by solving the system (5) on an analog computer. In the case of pulsed chemical pumping the generation consists of a single signal (Fig.9*a*): the parameter M_z quickly reaches the generation threshold, and then the transverse component $M_\perp$ appears. The relationship between M_z and $M_\perp$ (the phase diagram of the nuclear magnetisation) consists of a single loop (see insert in Fig.9*a*). In this case the chemical pumping pulse is accompanied by a single generation pulse.

With strong and sustained chemical pumping the radio-frequency emission takes the form of a regular series of pulses (Fig.9*b*). During the intervals between the pulses the chemical reaction in the system continues to create magnetisation, which reaches the generation threshold after some time. The phase diagram consists of many superimposed loops. This generation regime was demonstrated in Fig.8 (the chemical "pulsar"). If the rate of chemical pumping is lowered the pulse regime may change into continuous steady-state generation (see experiment in Fig.5).

In decaying reactions, i.e. with damped chemical pumping, we observe a smooth transition from one generation regime to the other (Fig.9*c*): the pulsed generation regime changes to continuous generation, which in turn decays as the chemical reaction comes to an end. Depending on the kinetics of the chemical reaction, i.e. on the kinetics of the chemical pumping of the Zeeman reservoir, different generation regimes can be established. Several of these have been demonstrated experimentally (see Section IV).

We have so far discussed only the radiation generated in a reacting system located in the coil of a tuned oscillator circuit. However, excitation of a chemically induced radio-frequency field is possible, in principle, even in the absence of special resonance circuits, i.e. in "free" space. The conditions for excitation of this type have been studied[15], and the generation threshold was found to be determined by the condition

$$|M_z| v = \frac{3c^3}{2\gamma_n T_2 \omega_L^3} \ , \qquad (8)$$

where ν is the volume of the sample containing the polarised reaction products, and T_2 is the characteristic time for the "disruption" of the coherence. From formula (8) we can obtain the minimum volume ν_{min} of reaction products with the maximum nuclear polarisation coefficient consistent with self-excitation of the precession in free space. For a concentration of polarised protons $N = 10^{-2}$ mole litre^{-1}, $T_2 = 10$ s, and $f_L = \omega/2\pi = 100$ MHz, we find that $\nu_{min} \cong 10$ litre. If we increase the frequency, ν_{min} decreases as ω_L^{-3}.

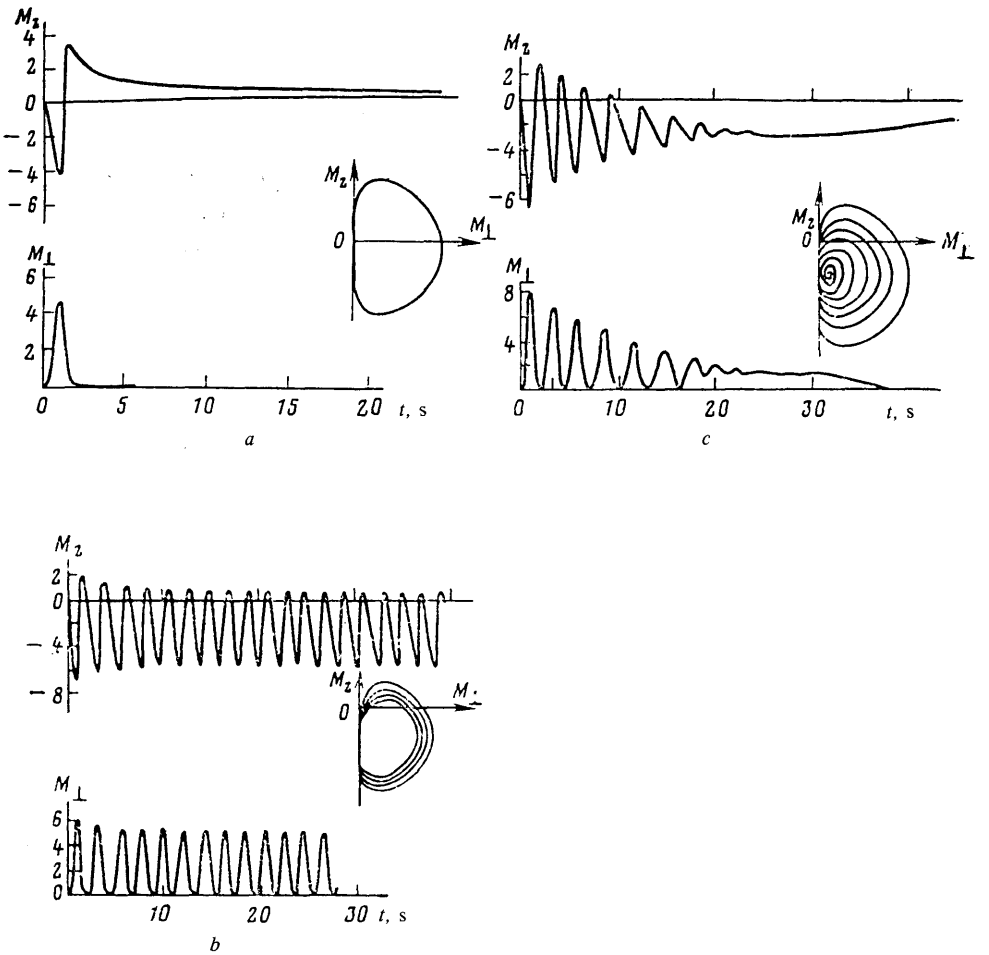


Figure 9. Radio-frequency generation dynamics of the chemical raser: *a*) for a fast reaction, *b*) for a reversible photochemical reaction, *c*) for a slow unimolecular reaction. In each case the "phase diagram" of the nuclear magnetisation in $M_\perp$, M_z coordinates is shown as an insert. The intensity of radio emission is proportional to $M_\perp^2$.[13]

Throughout this review we have dealt with the radio-frequency emission generated by the precessing total magnetic dipole of chemically polarised nuclei. The electromagnetic field of this type of dipole can be arbitrarily divided into three components[16]: the short-range field, decreasing as R^{-3} (where R is the distance from the source); the intermediate range field, decreasing as R^{-2}; the long-range field, decreasing as R^{-1}. In all the experiments discussed above the short-range region was detected. The electromagnetic field in the long-range region (which is often assumed to be the relevant region in discussion of radio emission) has not so far been experimentally explored because its strength is very low. However, in principle this field can be observed by using extremely sensitive instruments (similar to those employed in radio astronomy).

VI. CHEMICAL "RADIO RECEIVER"

We have shown that a chemical reaction can generate r.f. radiation. It is therefore legitimate to ask whether, conversely, r.f. radiation can affect chemical reactions, or in other words whether a chemical reaction can act as a receiver and detector of radio emission. An answer in the affirmative is suggested by the known effect of a radio-frequency field on the spin systems of reacting species, which can alter the rate of a chemical reaction or the yield of products by allowing previously spin-forbidden transitions. Several experimental realisations of this type of "chemical" radio receiver have been described.

A clear example is the effect of an electromagnetic field on reactions involving paramagnetic species (radicals and triplet excitons) in solids[17-20]. Using this phenomenon

(i.e. the sensitivity of the elementary acts of chemical reactions to an external electromagnetic field) the authors[17–20] have developed a new radio-spectroscopic method of detecting paramagnetic intermediates in reactions, which they have called RYDMR (Reaction Yield Detected Magnetic Resonance).

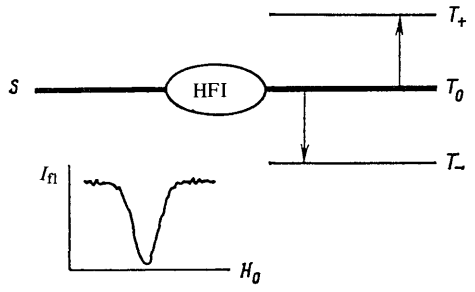


Figure 10. Principle of detection by the RYDMR spectrum, recorded for the fluorescence of the molecules formed in ion-radical recombination reactions. The hyperfine interaction (HFI) induces singlet–triplet transitions, and the external electromagnetic field at the ESR frequency induces a "loss" of radical pairs to the T_+ and T_- states. The result is an increased yield of triplet molecules, a decreased yield of singlet (fluorescing) molecules, and a decrease in the fluorescence intensity. The vertical arrows denote the transitions between T_0 and $T_\pm$ levels at the ESR frequency.

The basic idea of the method is shown in Fig.10. Assume that the interaction between two radicals (the cation M^+ and the anion M^-) takes place by electron transfer:

$$M^{\cdot+} + M^{\cdot-} \rightarrow (M^{\cdot+}M^{\cdot-}) \rightarrow M^* + M \ ,$$

so that one of the molecules (M*) is formed in an excited state. If the electron transfer occurs in a singlet ion-radical pair the excited M* molecule will be in a singlet (S) state, and it will fluoresce. In the ion-radical pair ($M^{\cdot+}M^{\cdot-}$) the hyperfine electron–nucleus interaction (HFI) induces singlet–triplet conversion of the pair into the T_0 state (see Fig.10), from which a triplet (non-fluorescing) M* molecule is obtained. The S–T_0 transitions are reversible, with characteristic times of 10^{-8}–10^{-10} s. If the ion-radical pair experiences a variable field which induces resonant transitions from the T_0 to the T_+ and T_- states, the decrease in the number of pairs in the T_0 state produces an increased "loss" of singlet pairs. The yield of singlet M* molecules falls, and the yield of triplets increases. The frequency of the field which produces a change in the relative yield of singlet and triplet product molecules corresponds to ESR transitions in the radical pair, and therefore the dependence of the intensity of fluorescence on the magnetic field H_0 can be used to detect the ESR spectrum of the ion-radical pair (optical detection of ESR). The decrease in fluorescence associated with the decreased number of singlet pairs occurs at resonance values of the steady magnetic field, for which the splitting of the levels (T_0–$T_\pm$) corresponds to the frequency of the oscillating field.

The RYDMR spectra of excited charge transfer complexes in molecular crystals were first obtained in this way[17]. In this case the external electromagnetic field affects the probability of transitions between spin states in a pair consisting of two triplets, and it alters the rate of annihilation of the triplets with formation of an excited singlet fluorescing molecule. The RYDMR spectra of the radical + triplet exciton pair have also been observed[21].

A method of obtaining the RYDMR spectra of ion-radical pairs in liquids has recently been developed[22,23], and the ESR spectra of various ion-radicals have been obtained. The RYDMR technique has been used also to investigate the nature of the ion-radical pairs formed in the primary act of photosynthesis[25].

Another application of the RYDMR technique is in the detection of the magnetic resonance spectra of short-lived pairs of paramagnetic species, and in the measurements of their lifetimes (10^{-6}–10^{-10} s). The method offers a high sensitivity, often several orders better than the sensitivity of traditional magnetic resonance methods. Thus in the RYDMR detection of ion-radical pairs in liquids by fluorescence measurements a sensitivity of 20–100 pairs in the sample has been claimed[22]. Some estimates of sensitivity are given in Ref.20: in particular, for the annihilation of a triplet pair in molecular crystals a variable field in which the amplitude of the magnetic component is $H_1 = 1$ Oe produces a change of 10^{-5} in the rate of the process. In general, in order to allow an electromagnetic field of amplitude H_1 to influence the spin state of a pair of paramagnetic particles during the lifetime τ of the pair, we must satisfy the condition

$$\gamma_e H_1 \tau \approx \pi \ , \qquad (9)$$

where γ_e is the gyromagnetic ratio of the electron. Thus for pairs with $\tau \simeq 10^{-8}$ s we need $H_1 \simeq 20$ Oe. The RYDMR effect is a consequence of the influence of an external electromagnetic field on the course of chemical reactions in a condensed phase, and it can be detected not only from changes in the yield of singlet and triplet molecules under the influence of a variable field, but also from the relative yields of recombination and dissociation products of the pairs, from photocurrents, etc.

Zhitnikov and coworkers[26–28] have shown that a resonant radio-frequency field can affect the elementary acts of chemical reactions in the gas phase (for example, the ionisation by collision of helium and alkali metal atoms). As in the previous examples this effect of the r.f. field can be explained by the presence of spin-forbidden physicochemical processes which can be controlled by varying the spin state of the interacting particles.

Consider, for example, the ionisation of helium atoms. In the ground state (1^1S_0) the helium atom is diamagnetic, since the spins of the two electrons are compensated and their orbital moment is zero. When excited (for example, by a high-frequency gas discharge) the helium atoms pass into a metastable triplet state (2^3S_1) characterised by a total electron spin $S = 1$ and a lifetime of several microseconds. The energy of the metastable state is 19.77 eV, and its ionisation potential is 4.7 eV. Under normal conditions one of the two helium atoms with triplet excitation passes into the ground state (as a result of inelastic collisions), and the other atom is ionised. This produces an electron–ion plasma, easily detected by changes in the luminescence and in the electrical conductivity of the medium. Irradiation of the sample with circularly polarised light in a magnetic field H_0 causes optical orientation of the metastable helium atoms, i.e. it favours the occupancy of one of the three Zeeman sublevels of the triplet state. Very high degrees of

polarisation can be achieved in this way, and a very large fraction of the excited helium atoms have their magnetic moments in the same orientation with respect to the field H_0.

Optical orientation is found to have a large effect on the ionisation of the atoms by the collision reaction

$$\mathrm{He}(2^3S_1) + \mathrm{He}(2^3S_1) \rightarrow \mathrm{He}(1^1S_0) + \mathrm{He}^+(1^2S_{1/2}) + e^- ,$$

where e^- denotes a free electron. The total spin of the particles formed by this reaction is 1. Therefore this reaction is forbidden by the law of spin conservation (i.e. the law of conservation of angular momentum) in the case of two colliding helium atoms with electron spins in the same direction, since their combined spin is 2. As a result of the spin requirement the polarised helium atoms can only undergo elastic collisions, which do not lead to ionisation (in spite of the energy gain offered by the ionisation process). Thus the polarisation of the helium atoms results in a decrease in the density of free electrons and helium ions. Experimentally this effect is detected as a decrease in electrical conductivity and in luminescence intensity of the electron–helium plasma following optical orientation of the atoms.

A radio-frequency field affects the collisional ionisation of helium atoms by inducing resonant transitions between the Zeeman sublevels of the triplet state, thus lessening the polarisation of the atoms. The result is an increase in the number of collisions between metastable helium atoms, whose electron spins are in different orientations and for which inelastic processes are "allowed", leading to ionisation of one of the atoms. Therefore a radio-frequency field should increase the experimentally observed electrical conductivity of an electron–helium plasma. Formally this phenomenon can be described by postulating an additional participant to the reaction, whose presence ensures equality of the total spins of the reacting and the resulting particles. The role of this additional particle (with a spin $S = 1$) is played by the quantum of the radio-frequency field, whose absorption causes reorientation of the electron spins of the metastable helium atoms.

Very interesting experiments[28] on the influence of radio-frequency fields on the collisional ionisation of optically oriented alkali metal atoms (e.g. rubidium or caesium), and of excited helium atoms, have been reported. Since the ionisation potentials of alkali metal atoms are much lower than the excitation energy of the helium atom, inelastic collisions in the gas phase usually cause ionisation of the metal atoms and deactivation of the helium atoms:

$$\mathrm{He}(2^3S_1) + \mathrm{Rb}(5^2S_{1/2}) \rightarrow \mathrm{He}(1^1S_0) + \mathrm{Rb}^+(4^1S_0) + e^- .$$

The total spin of the resulting Rb^+ ion, helium atom in the ground state, and free electron is 1/2. However, if the magnetic moments of the colliding helium and rubidium atoms have the same orientation their total spin is 3/2. Therefore if the colliding helium and rubidium atoms have parallel spins the inelastic collisions accompanied by ionisation are spin-forbidden. Collisional ionisation is possible only when the spins of the colliding atoms are pointing in opposite directions. Indeed, it is experimentally found that the concentration of free electrons and ions decreases when the helium and alkali metal atoms have the same orientation. Perturbing the polarisation of these atoms by the application of a resonant radio-frequency field increases the number of inelastic collisions and the concentration of electrons and ions, as shown by a change in the observed electrical conductivity of the plasma.

However, the effect of radio-frequency fields on the spin systems of colliding and interaction atoms is not merely to equalise the occupancies of the Zeeman and hyperfine levels: these fields also create coherence in the spin systems. As we showed in Section II, coherence implies the existence of transverse components of the total magnetisation vector, precessing at the Larmor frequency around the direction of the external field H_0. It so happens that this radio-frequency coherence has the same effect as orientation on the collisional ionisation (atom polarisation). Since the transverse components of the electron spins of the helium and rubidium atoms have different Larmor precession frequencies, they will periodically show a parallel orientation, and under these conditions their collisional ionisation is spin-forbidden, only elastic collisions are possible, and the electrical conductivity of the plasma decreases. After some time the spins of the helium and rubidium atoms are found to point in opposite directions (owing to the difference in precession frequency), collisional ionisation is no longer forbidden by the law of conservation of spin (or of its transverse component), and the electrical conductivity of the plasma increases. The two types of process (elastic and inelastic collisions) alternate at a frequency equal to the difference between the precession frequencies of the magnetic moments of the excited helium and rubidium atoms. As a result the electrical conductivity of the plasma is modulated at this difference frequency. These experiments[28] are the first demonstration of the effect of electromagnetic fields and of radio-frequency spin coherence on the elementary acts of chemical reactions.

Various examples of the influence of variable electromagnetic fields on the rate and direction of chemical reactions have been considered above. In every case the chemical reaction acts as a "receiver" of electromagnetic radiation. The physical explanation of the change in reactivity of the atoms, triplet molecules, and ions lies in the partial relief from spin restrictions given by the external radio-frequency field. Similar effects should be observed in the interaction of alternating electromagnetic fields with nuclear (as opposed to electronic) spin systems. Partial control of the rate and direction of a chemical reaction should be possible by using a radio-frequency field to modulate the nuclear spin state of the participating radicals or radical pairs.

VII. CHEMICAL RADIOPHYSICS

Chemically induced radio-frequency emission is a new phenomenon, which allows the radiophysical properties of radical reactions to be observed. These properties allow new approaches to the study of the reactions themselves, and they offer new (radiophysical) methods of detecting the radical steps. They also suggest new ways of designing technological devices such as magnetometers and masers in which the working substance is the product of a chemical reaction incorporating an inverted population of Zeeman levels.

Radio-frequency emission can be generated, in principle, in a system of negatively polarised electrons and radicals. The special features and properties of this chemically induced emission of the energy of the Zeeman electronic reservoir are discussed in Ref.16.

The self-excitation of the precession of the nuclear magnetisation vector and the development of coherence in the nuclear spin system of the reaction products are equivalent to a transition from a disordered to an ordered state, i.e. to a non-equilibrium phase transition (similar to a phase transition of the second kind). In this transition the quantity equivalent to the order parameter is the modulus of the transverse components of the precessing nuclear magnetisation vector of the reaction products. The

observations reported in Refs.2, 11, and 12 are the first examples of magnetic phase transitions caused by chemical reactions.

The discovery of chemically induced radio-frequency emission and of the effect of radio-frequency electromagnetic fields on the elementary acts of chemical reactions has laid the foundation of a new branch of science: chemical radiophysics, whose object is to study the generation and detection of radio waves at the chemical (molecular) level, to investigate the radiophysical properties of chemical reactions, and to analyse the chemical and radiophysical consequences of coherence effects in spin systems[29]. Radiophysical properties may also be found, in future, in biochemical reactions and processes.

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Metal Complexes of Porphine and Azaporphine Compounds as Catalysts of Reactions Involving Oxidation by Molecular Oxygen

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The results of studies of the catalytic action of the metal complexes of porphines and azaporphines in reactions involving oxidation by molecular oxygen are surveyed. Various mechanisms of the action of the metal-porphine catalysts are analysed and a relation between the characteristics of the structures of these compounds and the spectrum of their activity is demonstrated. In terms of the problem of the preparation of new catalysts for the selective oxidation of organic compounds under mild conditions, possible ways of seeking systems in which the metal-porphines function as oxygen transferring agents are outlined.
The bibliography includes 161 references.

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I. INTRODUCTION

Porphyrin compounds enter into the composition of many biologically important substances, including a series of oxidative enzymes such as oxidases, peroxidases, and others. The biological activity of porphyrins and their participation in a wide variety of the vital processes of living organisms have aroused much interest in these compounds[1-23]. The characteristic features of the structures of metalloporphines†, which consist of planar cyclic molecules with an extensive π-conjugation system, are responsible for their catalytic activity. In the planar molecules of metalloporphines the fifth and sixth coordination sites of the central metal ion are available for the coordination of the molecules of reactants in the reaction being catalysed and the extensive π-conjugation system facilitates a redistribution of the electron density within the reaction complex, which lowers the activation barrier to the reaction.

We believe that the problem of the modelling of the enzymtic catalytic activity of metalloporphyrins and of the formation on their bases of new catalytic systems for the oxidation of organic substrates under mild conditions, selective with respect to the reaction products, urgently requires solution at the present time. This review deals with the catalysis by metalloporphyrins of reactions involving oxidation by molecular oxygen in terms of the mechanisms of the action of the catalyst.

The studies on these lines were initiated by those of Cook[24-26] and Paquot[27-31] on metallophthalocyanines (M-Pc). Later these catalysts were investigated in other studies[32-68]. The synthesis of metallopolyphthalocyanines (M-Poly-Pc)[69,70] led to an interesting modification of phthalocyanine catalysts with a still more developed π-conjugation system and permitting the introduction of different metal ions into the same catalyst molecule. As a rule M-Poly-Pc exhibits a higher catalytic activity[37,71-80] than the corresponding monomeric analogues. The catalytic activity of metalloporphyrins (M-P) began to be studied comparatively recently[43,81-102], which is apparently due to their lower availability and lower stability compared with M-Pc.

The mechanisms of the catalysis by metalloporphines of oxidations by molecular oxygen have not as yet been finally elucidated. However, the available data show that metalloporphines can act via alternative mechanisms: via a donor mechanism in which an oxygen molecule is activated and via an acceptor mechanism in which the substrate undergoing oxidation is activated. A third mechanism, according to which metalloporphines catalyse the decomposition of the hydroperoxides present in the substrate undergoing oxidation in the form of impurities and thus initiate the free-radical chain auto-oxidation, is also discussed in the literature.

We shall consider each of these mechanisms in greater detail.

II. THE MECHANISM OF THE ACTIVATION OF OXYGEN

In the majority of systems[32-39,44,45,47,51,59-61,67,68,71,74-79,81,83,85,86,88-90,99-102] one is to some extent justified in postulating that molecular oxygen is coordinated to the metal ion of the metalloporphine and that either partial charge transfer from the catalyst to the oxygen,

$$P\text{-}M + O_2 \rightleftharpoons P\text{-}M^{\delta+} \ldots O_2^{\delta-},$$

or the transfer of one electron,

$$P\text{-}M + O_2 \rightleftharpoons P\text{-}M^{+} \ldots O_2^{\cdot-},$$

or two electrons,

$$P\text{-}M + O_2 \rightleftharpoons P\text{-}M^{2+} \ldots O_2^{2-},$$

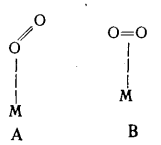
take place with formation of a superoxo- or peroxo-complex respectively.

Although direct evidence for the presence of metalloporphine-oxygen complexes in the catalytic reaction system has not so far been obtained, there are a number of indirect indications in support of the oxygen activation mechanism. One of these is the existence of 1:1 oxygen—metalloporphine complexes established by EPR and optical spectroscopy[103-125]. Under the influence of the field of the transition metal ion,

† The metalloporphine compounds include metalloporphyrins and metallophthalocyanines. The molecular skeleton of porphyrins is based on the porphyrin ring; phthalocyanines are derivatives of azaporphine.

the energy levels of the doubly degenerate antibonding π* orbitals of the oxygen molecule are split, the electrons are located at the more stable of the two orbitals, and their spins are paired; this entails the formation of a vacant orbital, which leads to the enhancement of the electron-accepting properties of the oxygen.

Two types of addition in mononuclear complexes of the type M...O_2 are known[126]: inclined terminal addition of oxygen in which the metal atom is linked to only one of the two oxygen atoms and the M–O–O angle is approximately 120° (A) and symmetrical addition of oxygen in which the metal is coordinated to the double bond of the oxygen molecule (B):



A B

In the first case a σ-bond is formed between one of the unshared electron pairs of oxygen and the vacant d_{z^2} orbitals of the metal and in the second it is formed between the occupied bonding π orbital of the oxygen molecule and the unoccupied d_{z^2} orbital of the metal. In both cases reverse donor interaction takes place with transfer of electron density from one of the doubly occupied d_{xz} (or d_{yz}) orbitals of the metal ion to the antibonding vacant π* orbital of the oxygen molecule, the reverse donor interaction predominating over the coordination σ-bonding, since the energy of the π* level of oxygen is lower than the energy of the *d* levels of transition metals.

The electronic configuration and the geometrical structure of the oxygen complexes of metalloporphines apparently depend both on the nature of the central metal ion[127] and on the nature of the porphin ring (Table 1). It is nowadays believed that the structure of the oxygen complexes of Co(II) Co(II)-porphyrins has been established[88,104,107–110,112]. These are octahedral complexes having one unpaired electron located at the coordinated oxygen. According to X-ray diffraction data, inclined terminal addition of the oxygen molecule occurs[115].

Three versions of the electronic structure are considered for the diamagnetic P-Fe...O_2 complexes[110,115,127,128]:

(1) $Fe^{2+}...O_2^*$—the oxygen molecule is present in the singlet state;

(2) $Fe^{2+}...O_2 \leftrightarrow Fe^{4+}...O_2^{2-}$—the quasi-neutral oxygen is involved in a resonance equilibrium with the peroxide ion;

(3) $Fe^{3+}...O_2^-$—a single electron of the iron ion is transferred to the oxygen molecule and the unpaired spins of the iron and oxygen electrons are paired.

The last two structures make it possible to explain the stabilisation of the oxygen complexes of Fe-P by polar solvents.

The oxygen complexes of Mn-P and Mn-Pc are pentacoordinate compounds. The peroxide structure TPP-$Mn^{4+}...O_2^{2-}$ has been proposed[119,120] for the tetraphenylporphine complex on the basis of the set of available experimental data (EPR and optical spectroscopy) and theoretical considerations, and symmetrical addition of oxygen was postulated by analogy with the peroxide complex of titanium-octaethylporphyrin[129]. The superoxide structure Pc-$Mn^{3+}...O_2^-$ has been proposed for the manganese-phthalocyanine complex[121–123].

In the case of Cr(II)-TPP(Py) irreversible addition of oxygen takes place. Infrared spectroscopic data indicate the superoxide structure of the complex $Cr^{3+}...O_2^-$,[130] while theoretical considerations indicate the peroxide structure $Cr^{4+}...O_2^{2-}$.[127]

The oxygen complex formed in the catalytic reaction system interacts with the substrate undergoing oxidation and as a rule initiates the free radical chain oxidation, but in certain cases the oxidation proceeds via a non-chain mechanism.

Table 1. The structure of the oxygen complexes of metalloporphines.

M-P	Structure	*S*	Geometry	References
Co(II)-TPP(Py)	$Co^{3+}...O_2^-$	1/2		[88, 104, 107—110, 112, 115, 127]
Fe(II)-P	$Fe^{2+}...O_2^*$ $Fe^{2+}...O_2 \leftrightarrow Fe^{4+}...O_2^{2-}$ $Fe^{3+}...O_2^-$	0		[110, 115, 127, 128]
Mn(II)-TPP	$Mn^{4+}...O_2^{2-}$	3/2		[119, 120, 127]
Mn(II)-Pc	$Mn^{3+}...O_2^-$	—	—	[121—123]
Cr(II)-TPP(Py)	$Cr^{3+}...O^-$ $Cr^{4+}...O_2^{2-}$	1		[130, 127]

Notation: *S* = overall spin quantum number; TPP = α, α′, α″, α‴-tetraphenylporphine; Py = pyridine.

$$[M\text{-}P]^{1/2},$$

Table 2. The composition (%) of the cyclohexene autoxidation products.

Catalyst	*t*, °C	Cyclohex-1-en-3-one	Cyclohex-1-en-3-ol	Epoxycyclohexane	References
Ni-Pc	65	69	24	7	[27]
Fe-TPP	25	73	24	3	[82]
Mn-TPP	25	80	18	2	[86]

1. Initiation of the Free-Radical Chain Oxidation

The set of facts such as the inhibition of the process by radical inhibitors[39,82,86,88], products characteristic of chain autoxidation (Table 2), and kinetic data indicate the initiation by metalloporphines of the free-radical chain autoxidation in the majority of systems.

Comparison of the experimental equations for the rates of oxidation of acetaldehyde, benzaldehyde, cyclohexene, and 2,5-dihydrofuran[75,77–79,85,88],

$$-d[O_2]/dt = k[RH]^{3/2}[O_2]^{1/2}.$$

where RH is the substrate undergoing oxidation, with the theoretical equation

$$-d[O_2]/dt = k_p/(2k_t)^{1/2} \quad (1)$$

obtained on the basis of the generally accepted mechanism of

chain autoxidation,

$$RH \xrightarrow{k_i} R^{\cdot},$$
$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot},$$
$$RO_2^{\cdot} + RH \xrightarrow{k_p} ROOH + R^{\cdot},$$
$$2RO_2^{\cdot} \xrightarrow{k_t} \text{non-radical products},$$

assuming a fairly long kinetic chain and a fairly high partial oxygen pressure, leads to an expression for the rate of initiation

$$v_i = k_i[RH][O_2][M\text{-}P],$$

which makes it possible to represent the initiation stage in the following manner:

$$P\text{-}M + O_2 \overset{K_{O_2}}{\rightleftharpoons} P\text{-}M^+ \ldots O_2^-,$$
$$P\text{-}M^+ \ldots O_2^- + RH \xrightarrow{k_i'} P\text{-}M^+ \ldots O_2H^- + R^{\cdot},$$

where K_{O_2} is the equilibrium constant of the reaction involving the formation of the oxygen complex (for brevity we shall refer to it as the oxygenation constant).

Table 3. The rate constants for the overall reaction and for the autoxidation chain initiation in systems catalysed by metalloporphines.

Substrate	Catalyst	t, °C	$10^3 k_p$, litre$^{3/2}$ × mol$^{-3/2}$ × s^{-1}	$10^3 k_i$, litre^2 × mol^{-2} × s^{-1}	Refs.
DHF	Co-T(p-CH_3-P)P	30	2.22—2.50	—	[85]
1-Methyl-CH	Co-T(p-CH_3-P)P	30	1.4 *	140	[85]
4-Methyl-CH	Co-T(p-CH_3-P)P	30	0.24 *	3.97	[85]
CH	Co-T(p-CH_3-P)P	30	0.158—0.184	7.67	[85]
1,3-CH-diene	CopT(p-CH_3-P)P	30	$6.4 \cdot 10^{-3}$ *	0.0414	[85]
Acetaldehyde	Co-T(p-CH_3-P)P	10	28	6	[88]
Benzaldehyde**	Co-T(p-CH_3-P)P	10	470—620	—	[79]
Acetaldehyde	Fe, Cu-poly-Pc	10	210 *	72	[78]
Acetaldehyde	Fe, Mo-poly-Pc	10	120 *	20	[78]
Acetaldehyde	Fe-poly-Pc	10	82*	11	[78]
Acetaldehyde	Fe, Co-poly-Pc	10	81 *	11	[78]
Acetaldehyde	Cu, Co-poly-Pc	10	11 *	0.017	[78]
Isobutyraldehyde	Fe, Cu-poly-Pc	10	450—670	—	[79]
Acroleine***	Fe, Cu-poly-Pc	40	—	66±2	[75, 77]

* Estimated by us from the data of Ohkatsu and Tsuruta[85] and Ohkatsu et al.[78] respectively.

** Solvent—ethyl isobutyrate.

*** Benzene, in the remaining cases—ethyl acetate.

Remarks: DHF = 2,5-dihydrofuran; CH = cyclohexane; CH-diene = cyclohexadiene; Co-T(p-CH_3-P)P = cobalt-tetra(p-tolyl)porphine; the equation for the rate of oxidation of acroleine is more complex than Eqn.(1), since in this case the rate-limiting stage is the reaction of the acyl radical with oxygen (this is associated with the stabilisation of the acyl radical of acroleine as a result of conjugation with the double bond); $k_i = k_i' K_{O_2}$.

The superoxide complex initiates the autoxidation chain, abstracting the mobile oxygen from the molecule of the substrate being oxidised. It is assumed[85] that the complex $P\text{-}M^+\ldots O_3^-$ can rupture C–H bonds whose energy does not exceed 79 kcal mole^{-1}. In the oxidation of unsaturated hydrocarbons there is also the possibility of the initiation of autoxidation by the addition of the superoxide complex to the double bond:

$$P\text{-}M^+\ldots O_2^- + \rangle C{=}C\langle \rightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{O-O-M^+-P}{C}}-.$$

The oxidation chain propagation and termination and the regeneration of the catalyst can be represented as follows:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \text{ (chain propagation)},$$
$$RO_2^{\cdot} + RH \rightarrow R^{\cdot} + ROOH$$
$$RO_2^{\cdot} + \rangle C{=}C\langle \rightarrow -\overset{|}{\underset{OOR}{C}}-\overset{|}{C}-$$
$$2RO_2^{\cdot} \text{ —non-radical products (chain termination)},$$
$$P\text{-}M^+\ldots O_2H^- \rightarrow M\text{-}P + HO_2^{\cdot} \text{ (catalyst regeneration)}.$$

The radical nature of the superoxide complex is manifested to a large extent in the chain oxidation reaction, which is indicated by the attack by the complex $P\text{-}M^+\ldots O_2^-$ on the hydrocarbon undergoing oxidation at the sites with maximum electron density[85].

The constants for the overall reactions and chain initiation have been estimated for a number of systems (Table 3).

2. Catalysis of Non-Chain Oxidation

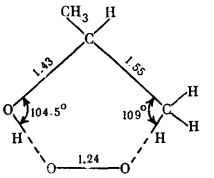
Data on the catalysis of non-chain oxidation by metalloporphines are of special interest for the solution of the problem of the selective oxidation of organic substrates by molecular oxygen.

The reverse donor interaction observed in the formation of an oxygen-metalloporhine complex, consisting in the transfer of electron density from one of the occupied d orbitals of the central metal ion to the antibonding vacant π^* orbital of the oxygen molecule, weakens the O–O bond, which is indicated by the increase of the distance between the oxygen atoms in the complex to 1.24–1.26 Å compared with the corresponding distance of 1.2074 Å in the free O_2 molecule[126]. The interaction with the substrate being oxidised can entail the complete rupture of the weakened O–O bond and the oxidation of the substrate either as a result of the insertion of an oxygen atom in the substrate molecule or as a result of the abstraction of hydrogen atoms from the latter[131,132].

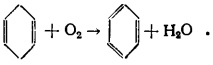
The second mechanism has been put forward for the gas-phase oxidation of propan-2-ol and propane-2-thiol, catalysed by M-Pc (M = Cr, Mn, Fe, Ni, or Cu) at 200–400 °C:[51,59,60]

$$CH_3{-}CHOH{-}CH_3 + {}^1/_2O_2 \rightarrow CH_3{-}CO{-}CH_3 + H_2O,$$
$$2CH_3{-}CHSH{-}CH_3 + {}^1/_2O_2 \rightarrow (CH_3)_2{-}CHSSCH{-}(CH_3)_2 + H_2O.$$

The following geometrical structure of the transition complex in the reaction has been suggested for the oxidation of propanol[59] (the bond lengths are given in ångstroms):



The oxidative dehydrogenation of cyclohexadiene by atmospheric oxygen, catalysed by M-Pc (M = Fe, Co, Ni, Cu, or Zn) at 250 °C, takes place analogously[19]:



The complex salts of certain porphyrins enter into the composition of oxidative enzymes as coenzymes. The attempts to model enzymic catalytic activity were unsuccessful for a long time—only radical chain autoxidation was observed. However, reports have now appeared that in certain homogeneous liquid-phase systems metalloporphines can function as agents transferring oxygen to the substrate being oxidised.

Data have been presented concerning the modelling of the functions of the monoxygenating enzyme cytochrome P.450 [81, 86,92,98] capable of catalysing the hydroxylation of saturated and aromatic hydrocarbons and the epoxidation of unsaturated hydrocarbons in the cells of living organisms. The coenzyme of cytochrome P-450, namely haemin, contains cysteine as an axial ligand. The maintenance of the enzyme in the reduced state is achieved as a result of the functioning of the microsomal respiratory chain[133].

The following modelling systems have been proposed:

(1) Iron-protoporphyrin (haemin) and an excess of thiosalicylic acid for the oxidation of cyclohexane by atmospheric oxygen in an aqueous acetone medium (the reaction products are cyclohexanol and cyclohexanone in proportions of 2 : 1); [81]

(2) TPP-MnCl and an excess of sodium tetrahydroborate for the oxidation of cyclohexane by atmospheric oxygen in a benzene-ethanol mixture (the reaction products are cyclohexanol and cyclohex-2-en-1-ol in proportions of 4 : 1); [86]

(3) TPP-MnCl–H_2–colloidal platinum in benzene with added imidazole or its derivatives for the oxidation of cyclohexene to epoxycyclohexane and cyclohex-2-en-1-one in proportions of 15 : 1 and of adamantane to adamantan-1-ol, adamantan-2-ol, and adamantan-2-one in proportions of 14.7 : 1.7 : 1; [98]

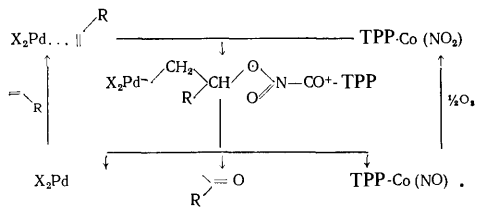
(4) haem-NAD (or NADP) for the hydroxylation of aniline in an alkaline medium (pH > 11) with formation of *p*-aminophenol[92] (NAD = nicotinamide-adenine dinucleotide; NADP = nicotinamide-adenine dinucleotide phosphate).

These systems contain an excess of the reducing agent, have products whose composition is characteristic of autoxidation, and are insensitive to the action of radical inhibitors.

It has been suggested[81,86] that one of the atoms of the oxygen molecule activated by the metalloporphyrin is capable of being inserted in the C–H bond on interaction with an unsaturated hydrocarbon, forming an alcohol, while in the reaction with an olefin it adds to the double bond, forming an epoxy-compound. It has been assumed[98] that the complex TPP-MnO, analogous to that observed in the M–P–iodosobenzene oxidising systems[134–141], is the hydroxylating and epoxidising species. When sodium tetrahydroborate is used as the reductant, the primary oxidation product is epoxycyclohexane, which is reduced by the excess $NaBH_4$ is cyclohexanol.

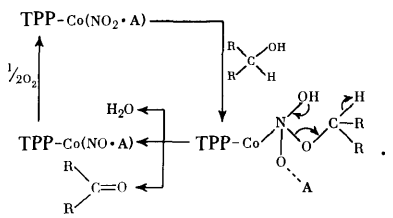
The TPP-MnCl–$(NBu_4)BH_4$ system in solution in methylene chloride catalyses the selective oxidation of olefins (cyclooctene, styrene, oct-1-ene, and phenylprop-1-ene) to the corresponding ketones, which are partly reduced by the excess $(NBu_4)BH_4$ to alcohols[98]. The products of the oxidation of cyclohexene are cyclohexanol and cyclohex-2-en-1-ol in proportions of 2 : 1.

Nitro- and nitroso-complexes of Co-TPP, namely (Py)Co-TPP(NO_2) and Co-TPP(NO), were used as oxygen transferring agents in a new catalytic system proposed for the selective oxidation of olefins: ethylene and propene were oxidised to acetaldehyde and acetone respectively[87]. The nitro-complex can be formally regarded as a species containing the monoanionic ligand $Co^+...NO_2^-$, capable of functioning as a weak nucleophile. In order to activate the olefin undergoing oxidation with respect to nucleophilic attack, it was coordinated to bivalent palladium. One of the oxygen atoms in the NO_2 ligand is then apparently transferred to the olefin and the resulting nitroso-ligand is oxidised by the oxygen supplied to the system in accordance with the scheme

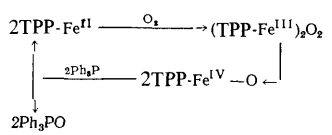


where X is the palladium counterion.

In the presence of Lewis acids [$BF_3.(C_2H_5)_2O$; $LiPF_6$], the complexes (Py)Co-TPP(NO_2) and Co-TPP(NO) also catalyse the selective oxidation of primary and secondary alcohols: benzyl alcohol and cycloheptanol are oxidised to an aldehyde and a ketone respectively[97]. It has been suggested that the Lewis acid (A) is coordinated to the oxygen of the nitro-group, increasing its electrophilicity. The oxidation can proceed via the formation of an ether-like intermediate which decomposes via a non-radical mechanism into a carbonyl product, water, and a nitroso-complex of Co-TPP:



Yet another pathway leading to the activation of oxygen is observed in the oxidation of triphenylphosphine catalysed by Fe-TPP in solution in toluene at 25 °C.[91] In the presence of molecular oxygen Fe-TPP is oxidised to the bridged peroxo-dimer $(TPP\text{-}Fe)_2O_2$, the first stage of the spontaneous decomposition of which involves the formation of the oxo-complex TPP-Fe^{II}–O. This complex is in fact the agent transferring oxygen to the Ph_3P molecule:



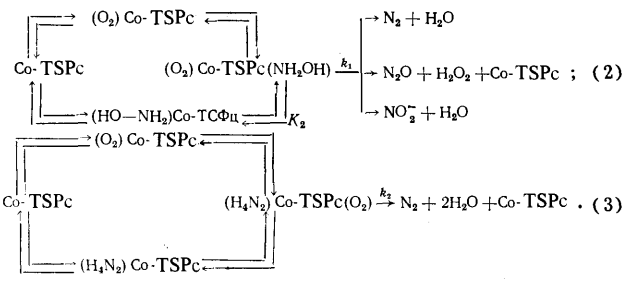
However, the oxo-complex also reacts with $(TPP\text{-}Fe)_2)_2$ and TPP-Fe...O_2:

$$TPP\text{-}Fe^{IV}\text{—}O + (TPP\text{-}Fe)_2O_2 \rightarrow (TPP\text{-}Fe)_2O + TPP\text{-}Fe...O_2 ,$$
$$TPP\text{-}Fe^{IV}\text{—}O + TPP\text{-}Fe...O_2 \rightarrow (TPP\text{-}Fe)_2O + O_2 ,$$

which leads to the deactivation of the catalyst and the cessation of the reaction; in the inactive reaction system the porphyrin compound is present only in the form of the bridged oxo-dimer. A conclusion concerning the mechanism of the oxidation of Ph_3P was reached on the basis of the analysis of the kinetics of the spontaneous decomposition of $(TPP\text{-}Fe)_2O_2$ and its reduction by Ph_3P.

The oxidation of hydroxylamine and hydrazine, catalysed by cobalt-tetrasulphophthalocyanine (Co-TSPc) in an alkaline medium, proceeds, according to Wagnerova et al.[67,68], within the coordination sphere of the ternary complex of Co-TSPc with O_2 in the substrate formed in the first stage of the

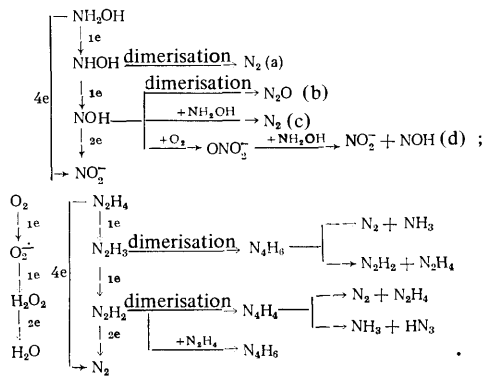
reaction:



This is supported by a series of facts. In an alkaline medium Co-TSPc forms a 1:1 complex with N_2H_4. The addition of hydrazine to the oxygen complex of Co-TSPc, which has two absorption bands at 626 and 670 nm, leads to their disappearance and the appearance of new bands at 450 and 680 nm. Subsequent passage of oxygen restores the initial spectrum.

The change of the reaction order with respect to N_2H_4, NH_2OH, and O_2 from 1 to 0 with increase of the reactant concentration also shows that N_2H_4, NH_2OH, and O_2 react in the coordinated state and the theoretical rate equations, derived for mechanisms (2) and (3), agree with the experimental equations. The constants $k_1 = 25\ s^{-1}$ and $k_2 = 2.0 \times 10^3$ have been estimated for hydroxylamine.

Analysis of the products of the oxidation of NH_2OH and N_2H_4 shows that the process takes place within the coordination sphere of the complex without the release of free radicals into space. The states in the successive oxidation of substrates and the reduction of oxygen are presented below together with their possible subsequent reactions, regardless of whether they are free radicals or enter into the composition of the complex:



If after the transfer of one or two electrons the radicals formed pass into space, then the NH_2OH oxidation products should contain more of the radical dimerisation products, in particular N_2O, and, as a result of the competing reaction (c), the relative NO_2^- content should increase or remain unchanged with increase of the initial NH_2OH concentration. In reality, the main NH_2OH oxidation product is NO_2^- (60%) and the amount of N_2O formed is very small. Furthermore, an increase of the initial NH_2OH concentration leads to a decrease of the relative content of NO_2^- in the products. All these findings support electron transfer within the complex. Molecular nitrogen is formed[68] when the complex Co-TSPc.(NOH) interacts with NH_2OH:

$$\text{Co-TSPc(NOH)} + NH_2OH \rightarrow N_2 + 2H_2O + \text{Co-TSPc} \quad .$$

Similarly the presence of only traces of ammonia, the radical recombination product, in the hydrazine oxidation products also indicates an intracoordination mechanism of electron transfer.

The electron transfer from the substrate to oxygen probably proceeds via the central cobalt ion with participation of the π-electron system of the phthalocyanine ring and the process can proceed in more than one stage.

Despite the fundamental similarity of the mechanisms of the oxidation of NH_2OH and N_2H_4 in the presence of Co-TSPc, the detailed electron transfer mechanisms are apparently different. Thus the amount of hydrogen peroxide formed in the oxidation of hydrazine increases in the course of the reaction, which can be explained by assuming that the oxidation proceeds in two stages, i.e. that oxygen displaces H_2O_2 from the intermediate ternary complex:

$$\text{(O}_2\text{) Co-TSPc(N}_2\text{H}_4\text{)} \rightarrow \text{(H}_2\text{O}_2\text{) Co-TSPc(N}_2\text{H}_2\text{)} \rightarrow$$
$$\xrightarrow{O_2} \text{(O}_2\text{) Co-TSPc(N}_2\text{H}_2\text{)} \rightarrow H_2O_2 + N_2 + \text{Co-TSPc} \quad .$$

According to our data[99-101], the oxidation catalysed by metalloporphyrins in an aqueous medium involves the generation of a free superoxide radical-anion. One can put forward two possible mechanisms:

(1) dissociation of the oxygen complex of the metalloporphyrin with formation of O_2^-:

$$\text{P-M}^+ \ldots O_2^- \rightleftarrows \text{P-M}^+ + O_2^- \quad ;$$

(2) electron transfer from the substrate S undergoing oxidation to oxygen within the coordination sphere of the ternary complex of M-P with O_2 and S:

$$\text{S}\ldots\text{M-P}\ldots O_2 \rightarrow \text{M-P} + S^+ + O_2^- \quad .$$

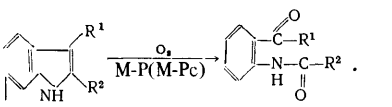
The first reaction involves the formation of the oxidised form of the catalyst and the completion of the catalytic cycle requires a catalyst regeneration stage via the interaction with the substrate or with one of the intermediate products of the reaction.

A typical example of the process with a "superoxide" mechanism is the oxidation of adrenalin in an aqueous medium, catalysed by porphyrin complexes of cobalt: Co-α, α', α'', α'''-tetra(*p*-sulphophenyl)porphine and Co-mesoporphyrin[99,100]. The oxidation process is inhibited by superoxide dismutase and is not catalysed by metal-free porphyrins. The kinetic data indicate the operation of the first mechanism in this system and the catalyst is regenerated via the reaction with the peroxide ion O_2^{2-}:

$$\text{Co}^+\text{-P} + O_2^{2-} \rightarrow \text{Co-P} + O_2^- \quad .$$

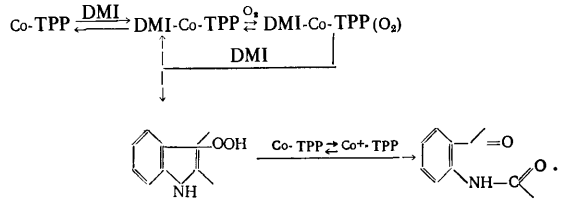
The coordination of the substrate to the metalloporphyrin is not essential in all cases. This is indicated by the catalysis of the oxidation of the Fe^{2+} ion (a substrate which cannot behave as an axial ligand) by cobalt-porphyrin to Fe^{3+}.[102]

The dimethyl ether of metalloprotoporphyrin TPP-M (M = Co, Cu, or Ni) in solution in methylene chloride[83,95] and Mn-Pc in solution in dimethylformamide (DMF)[142] catalyse the dioxygenation of alkyl derivatives of indole with formation of the corresponding ketoamides:



The formation of a ternary complex of the catalyst with O_2 and indole is indicated by the results of ultraviolet spectroscopic and EPR studies. In the case of Mn-Pc, it has been suggested[142] that one such complex of an indole derivative interacts with the oxygen of another complex—the reaction is of second order with respect to Mn-Pc. In the case of

Co-TPP it is believed[95] that the interaction of the ternary complex with a dimethyl indole (DMI) molecule results in the formation of 2,3-dimethylindolyl hydroperoxide—its presence in the reaction system has been demonstrated by NMR. The next reaction stage involves the decomposition of the hydroperoxide, which is also catalysed by Co-TPP:



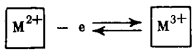
It must be emphasised that the study of the non-chain oxidation processes in the presence of metalloporphines is of great interest from the standpoint of the understanding of the mechanisms of the operation in biological systems of oxidative enzymes containing porphyrin structures. Another important aspect of these investigations is the creation of new catalytic systems for the selective non-chain oxidation of organic compounds by molecular oxygen under mild conditions. We believe that investigations where the reaction is carried out in the presence of a suitable reductant capable of regenerating the catalyst in the course of the reaction and which involve, together with the activation of molecular oxygen on the metalloporphine, the additional activation of the substrate being oxidised with respect to nucleophilic attack by its coordination to a suitable complex-forming agent are the most promising. Bimetallic porphine systems containing electron-donating and electron-accepting active centres may prove to be effective for the simultaneous activation of oxygen and the substrate being oxidised.

3. The Influence of Various Factors on the Catalytic Activity of Metalloporphines

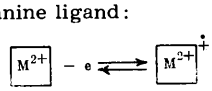
It is of interest to compare the influences of various factors—the nature of the metal, the porphine ring, and the trans-ligand —on the catalytic activities of metalloporphine compounds and on their oxygen affinity (K_{O_2}) in systems involving the oxygen activation mechanism. When oxygen complexes are formed by metalloporphines, electron density is transferred to the oxygen molecule and the oxidation potential of the latter can be conveniently selected as the parameter characterising the influence of the above factors on the properties of M-P.

(a) *The nature of the metal.* Table 4 shows that the lower the oxidation potential of the metalloporphine M-P, the higher its oxygenation constant K_{O_2}. Mn-TPP, for which K_{O_2} is smaller by several orders of magnitude than might have been expected on the basis of the potential, is an exception. This may be associated either with the fact that the oxygen complex of Mn-TPP has a peroxide structure, in contrast to the superoxide complexes of other metalloporphyrins M-P or with the fact that the complex Mn-TPP(O_2) is tetrahedral, while the complexes of other metalloporphyrins M-P are octahedral (it has been shown for Co-porphyrins that the electron-donating *trans*-ligands greatly accelerate the oxygenation[109]).

We shall follow the influence of the nature of the metal on the catalytic activity of metalloporphines in various systems. In the oxidative dehydrogenation of cyclohexadiene by atmospheric oxygen at 250 °C, a clear-cut correlation can be traced between the oxidation potentials of the metallophthalocyanines M-Pc and their activity (Fig.1). For the series of metals Fe, Co, Ni, Cu, and Zn, the oxidation potentials of Mn-Pc as well as M-TPP (Table 5) have a maximum at the point corresponding to Ni, which is associated with the change in the oxidation mechanism. The iron and cobalt complexes are oxidised via the central metal ion:



and the copper and zinc complexes are oxidised via the porphyrin or phthalocyanine ligand:



(The rectangle denotes a π-electron porphine system).

Table 4. The oxidation potentials $E_{1/2}$ of the metalloporphyrin complexes[143] and their oxygenation constants at −78 °C.[115]

Complex		$\lg K_{O_2}$	$E_{1/2}$, V
Co-TPP(Py)	(in toluene)	−1.7	+0.13
Co-T(p-OCH_3-P)P(N-CH_3-Im	(in toluene)	−0.8	+0.11
Fe-T(piv-P)P(N-CH_3-Im)	(solid)	6 4	−0.11
Mn-TPP	(in toluene)	~2.1	−0.27
Cr-TPP(Py)	(solid)	*	−0.86

* Cr-TPP(Py) combines irreversibly with O_2.

Remarks: K_{O_2} is expressed in mm^{-1}; $E_{1/2}$ is the potential measured in DMSO relative to the saturated calomel electrode; T(piv-P)P = meso-tetra(α, α', α'', α'''-*O*-pivalimidophenyl)porphine; N-CH_3-Im = *N*-methylimidazole.

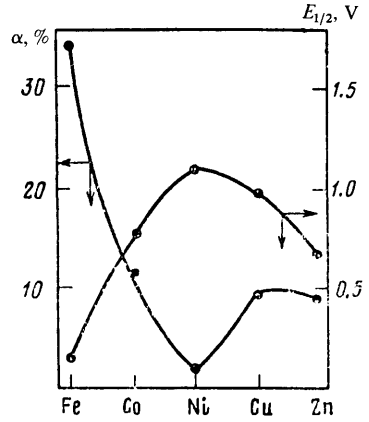


Figure 1. Dependence of the catalytic activity (α is the degree of conversion) in the oxidative dehydrogenation of cyclohexadiene by air and of the oxidation potentials $E_{1/2}$ of M-Pc on the nature of the central metal ion[19].

In the case of nickel both processes take place at the same potential.

The catalytic activity of metalloporphines varies in opposition to the oxidation potentials and is a minimum for Ni-Pc; Cu-Pc exhibits a higher catalytic activity than might have been expected on the basis of its oxidation potential. A similar anomaly has been also observed in other systems. This is apparently associated with the specific features of the interaction of copper complexes with molecular oxygen. The nature of this interaction in terms of the electronic structure can only be postulated, but it is striking that the most important metalloenzymes, catalysing the reduction of oxygen in biological systems, contain iron and copper.

Table 5. The first oxidation potentials of metalloporphines (OEP = octaethylporphyrin) relative to the saturated calomel electrode (in volts).

M	Electronic configuration of M	TPP (Ref.143)	TPP* (Ref. 144, 145)	OEP (Ref.143)	Pc** (Ref. 144, 145)
Cr^{2+}	d^4	−1.06 ***	—	−1.14 ****	—
Mn^{2+}	d^5	−0.23 *****	—	−0.42 ****	−0.11
Fe^{2+}	d^6	−0.19 ****	−0.32	−0.24****	+0.16
Co^{2+}	d^7	+0.32	+0.52	—	+0.77
Ni^{2+}	d^8	+1.04	+1.01	+0.73	+1.10
—	—	+0.95	+1.00	+0.81	—
Cu^{2+}	d^9	+0.90	+0.99	+0.79	+1.00
Zn^{2+}	d^{10}	+0.71	+0.78	+0.63	+0.68

* In benzonitrile.

** In 1-chloronaphthalene.

*** In methylene chloride.

**** In DMSO.

***** In acetonitrile. In the remaining cases the solvent was butyronitrile.

Table 6. Data on the oxidation of indole derivatives in solution in methylene chloride[83,95].

Catalyst	$E_{1/2}$, V	3-Methylindole		2,3-Dimethylindole	
		τ, h	α, %	τ, h	α, %
Co-TPP	+0.32	5	70	1	50
Ni-TPP	+1.04	20	traces	20	traces
Cu-TPP	+0.90	20	50	3	40

Remarks: The values of $E_{1/2}$ in butyronitrile[143] are quoted relative to the saturated calomel electrode; τ = reaction time; α = conversion of substrate.

The activity of M-TPP in the liquid-phase oxidation reactions of indole derivatives is also correlated with the oxidation potential of the catalyst and is a minimum for Ni-TPP (Table 6). In the oxidation of adrenalin in an alkaline medium, Co-T(*p*-sulpho-P)P is also more active than Ni-T(*p*-sulpho-P)P.[99]

Co-TPP deviates (is less active) from the correlation between the catalytic activity of M-TPP in the acetaldehyde oxidation reaction (Table 7) and their oxidation potentials.

In the gas-phase oxidation of propane-2-thiol and propan-2-ol at 250–350 °C, manganese-phthalocyanine exhibits a lower activity (Table 8) than suggested by its oxidation potential. This can be associated with the oxidation of the Mn^{2+} ion at high temperatures[146]. The copper complex shows, as usual, an anomalously high activity. Ni-Pc is more active in the oxidation of propanol than might have been expected. In order to account for the activity series obtained for metallophthalocyanines, the authors resorted to the molecular orbital and ligand field theories[51,61].

(b) *The nature of the porphine ring.* It follows from Table 9 that the greater the basicity (the quantity bearing an inverse relation to pK_a) of the free porphyrin base, the lower the oxidation potential of the corresponding metalloporphyrin and the higher its oxygen affinity. Octaethylporphyrin (OEP) is an exception.

Table 7. Kinetic data for the autoxidation of acetaldehyde (0.5 M) in solution in ethyl acetate catalysed by M-TPP (5×10^{-3} M at 10 °C).[89]

Catalyst	$E_{1/2}$, V	$-10^6\, d[O_2]/dt$, mol litre^{-1} s^{-1}	$10^6\, k_i$, litre^2 × mol^{-2} s^{-1}
Mn-TPP	−0.23	3.5	11.2
Co-TPP	+0.32	2.6	6.2
Ni-TPP	+1.04	3.1	8.8
Cu-TPP	+0.90	3.4	10.6

Remarks: The potentials $E_{1/2}$ in butyronitrile[143] (in acetonitrile for Mn-TPP) are quoted relative to the saturated calomel electrode; the k_i were estimated from the data of Ohkatsu and Osa[89].

Table 8. The activation energies (kcal mole^{-1}) for the gas-phase oxidation reactions of propanol and propanethiol catalysed by M-Pc.[51,59–61]

M	Mn	Fe	Co	Ni	Cu	Zn
$E_{1/2}$, V	−0.11	+0.16	+0.77	+1.10	+1.00	+0.68
Propane-2-thiol	15—18	12—14	16—20	30	14—17	23—28
Propan-2-ol	15	10	23	14	9	—

Remarks: The potentials $E_{1/2}$ in 1-chloronaphthalene[144,145] are quoted relative to the saturated calomel electrode.

An analogous relation is observed also between the catalytic activity of metalloporphines and the basicity of the corresponding porphine bases. Thus the cobalt complex of the more basic dimethyl ether of protoporphyrin (Co-DME-proto-P) is a more active catalyst of the oxidation of indole derivatives [3-methylindole (I), 3-methoxypropionylindole (II), and 3-methoxybutyrylindole (III)] than the corresponding complex of the less basic TPP (Table 10). The catalytic activity of tetrasubstituted copper-phthalocyanines in the cumene oxidation reaction at a temperature below 100 °C increases with enhancement of the π-donor properties of the substituents: $NO_2 < C_5H_5N < H < Br < Cl$.[36]

(c) *The nature of the substituents in the phenyl groups of tetraphenylporphine.* The electron-donating and electron-accepting properties of *para*-substituents in the phenyl groups of Co-TPP have a weak influence on its oxidation potential[143] and oxygenation constant[148] (Table 11), which is apparently associated with the fact that the benzene rings

are arranged at right angles to the plane of the porphyrin nucleus and do not therefore contribute significantly to its π-conjugation system.

Table 9. The influence of the basicity of the free porphyrin base on the oxidation potential of Mn-P [146] and the oxygenation constant of Co-porphyrins (−45 °C). [147]

Porphyrin ligand	pK_a	$E_{1/2}$, V	Im	Py	Pip	N-CH_3-Im
OEP	6	—	24.5	1.41	1.78	23.4
DME-meso-P	5.8	−0.19	32.4	—	—	—
DME-deutero-P	5.5	−0.14	—	—	—	—
DME-proto-P	4.8	−0.11	14.4	14.4	4.47	20.0
T(*p*-OCH_3-P)P	>3	—	—	0.76	1.4	6.5
TPP	~3	+0.01	1.58	—	—	—

Remarks: K_a = dissociation constant of the protonated free porphyrin base: $H_3\text{-}P \rightleftarrows H^+ + H_2\text{-}P$; the potentials $E_{1/2}$ in acetonitrile are quoted relative to the standard hydrogen electrode; the values of 10^3 K_{O_2} (mm^{-1}) are quoted in the remaining columns for different axial ligands in solution in toluene; Pip = piperidine.

Table 10. Data on the oxidation of indole derivatives in solution in methylene chloride[83,95].

Substrate oxidised	Catalyst	τ, h	α, %
(I)	Co-DME-proto-P	3	80
(I)	Co-TPP	5	70
(II)	Co-DME-proto-P	20	40
(II)	Co-TPP	30	50
(III)	Co-DME-proto-P	18	40
(III)	Co-TPP	24	60

Table 11. The influence of the substitutents X in Co-T(*p*-X-P)P on $E_{1/2}$, [143] K_{O_2} at −38 °C, [148] and the catalytic activity in the acetaldehyde (0.5 M) oxidation reaction in solution in ethyl acetate at 10 °C. [89]

X	$E_{1/2}$, V	$\lg K_{O_2}$	$-10^6\, d[O_2]/dt$, mol litre^{-1} s^{-1}
OCH_3	0.33	1.65	4.2
CH_3	0.35	1.61	81.0
H	0.39	1.48	2.8
Cl	0.40	1.45	1.2

Remarks: The values of $E_{1/2}$ in butyronitrile are quoted relative to the saturated calomel electrode; K_{O_2} (for Py)Co-T(*p*-X-P)P (mm^{-1}) refers to a solution in toluene; catalyst concentration 5×10^{-3} M; $P_{O_2} = 1$ atm.

The only reaction for which the influence of the nature of the substituents in the phenyl groups of the catalyst has been studied is the oxidation of acetaldehyde in the presence of Co-T(*p*-X-P)P. [89] The tetramethyl-substituted catalyst exhibits an anomalously high activity in this system (Table 11).

At the present time the above finding cannot be explained and the lack of data for other reactions would make premature any conclusions concerning the influence of the nature of the substitutent X in M-T(*p*-X-P)P on the catalytic activity.

(d) *The nature of the trans-ligand.* A general correlation between the basicity of the axial ligand L in the complex (L)Co-P and the oxygenation constant of the latter has not been observed[105,106,109,115,147] (Fig. 2). However, for a series of structurally similar axial bases [substituted pyridines (Fig. 2) and substituted phosphines[149]], a linear relation can be traced between K_{O_2} and pK_a. The lack of a general correlation is associated with the fact that the parameter pK_a characterises only the σ-donor properties of the ligand but does not take into account its π-donor properties. However, π-donor *trans*-ligands should enhance the reverse donor interaction of (L)M-P with O_2 and hence should increase its oxygen affinity. Indeed, Fig. 2 shows that powerful π-donors such as imidazole and DMF increase the oxygenation constant.

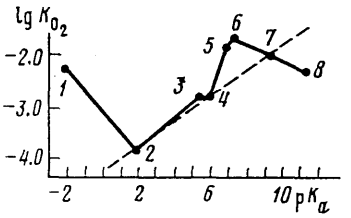


Figure 2. Relation between $\lg K_{O_2}$ (toluene, −45 °C) for (L)Co-DME-proto-P and the pK_a of the axial ligand L: [115] *1*) dimethylformamide; *2*) 4-cyanopyridine; *3*) pyridine; *4*) 4-butylpyridine; *5*) imidazole; *6*) 1-methylimidazole; *7*) 4-aminopyridine; *8*) piperidine.

Table 12. The values of K_{O_2} and the oxidation potentials of the complexes (L)Co-T(*p*-OCH_3-P)P. [147]

L	$-\lg K_{O_2}$	$E_{1/2}$, V
N-Methylimidazole	1.72	−0.48
4-Picoline	2.20	−0.23
5-Chloro-*N*-methylimidazole	2.26	−0.24
Piperidine	2.28	−0.31
3,4-Lutidine	2.35	−0.22
Pyridine	2.46	−0.20

Remarks: The values of K_{O_2} are expressed in mm^{-1} (obtained at −65 °C in toluene); the potentials $E_{1/2}$ were obtained in DMF; L = axial ligand.

In connection with the foregoing, it would apparently be more useful to compare the K_{O_2} with the oxidation potentials of the metalloporphyrins M-P having an axial ligand (Table 12). Despite the existing deviations, a general trend can be seen, namely an increase of the oxygenation constant with decrease of the oxidation potential of (L)Co-T(*p*-OCH_3-P)P.

The influence of electron-donating additives on the rate of the catalytic oxidation has been studied in a series of systems. The rate of oxidation of acetaldehyde catalysed

by Co-T(p-CH_3-P)P passes through a maximum as a function of the relative content of the additive (pyridine or DMF) corresponding to the ratio [additive]/[catalyst] = 1 (Fig. 3). It has been shown by EPR that, depending on the amount of added pyridine, a 1 : 1 or 1 : 2 Co-TPP-pyridine complex is formed. Consequently the axial base occupying the fifth coordination site in the catalyst molecule increases its catalytic activity. However, in the presence of large amounts of the additive, the latter occupies both coordination sites of the catalyst and prevents the coordination of oxygen, which lowers the rate of reaction.

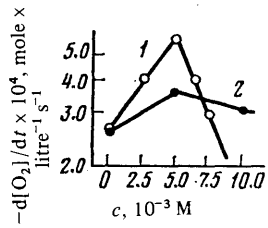


Figure 3. The influence of added pyridine (line *1*) and dimethylformamide (line *2*) on the rate of oxidation of acetaldehyde catalysed by Co-TPP in solution in ethyl acetate at 10 °C. [89]

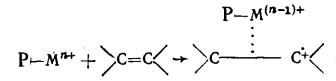
An analogous accelerating effect of basic additives (acetone, benzamide, urea, pyridine, acridine, aniline, and piperidine) has been demonstrated in the oxidation of benzaldehyde in the presence of Co-T(p-CH_3-P)P [89] and it has been shown that the higher the basicity of the additive the smaller its amount required to increase the rate of reaction.

It has been stated that catalytic amounts of pyridine have an accelerating effect in the oxidation of cumene in the presence of metallopolyphthalocyanines[74,75].

Thus analysis of data concerning the influence of various factors on the catalytic activity of metalloporphines reveals the following tendency: factors increasing the oxygenation constants of metalloporphyrins as a rule increase also their catalytic activity in oxidation reactions proceeding via an oxygen activation mechanism.

III. THE MECHANISM OF THE ACTIVATION OF THE SUBSTRATE UNDERGOING OXIDATION

In the systems examined above, metalloporphines function in accordance with a donor mechanism, transmitting electron density to the oxidant molecule. The presence of an extensive π-conjugation system in the metalloporphines, capable of stabilising different valence states of the central metal, gives rise to the possibility of the operation (under certain conditions) of an alternative mechanism of the catalysis—an acceptor mechanism characterised by partial or complete transfer of an electron from the oxidised substrate to the catalyst:



A similar mechanism has been postulated in the oxidation reactions of cyclohexene in solutions in nitrobenzene and benzene[84,93] and of squalene in solution in benzene[94] in the presence of Co(III)-OEP on the basis of the following data: firstly, the diamagnetic Co(III)-OEP cannot activate oxygen, since it does not form complexes with it, and, secondly, an EPR signal ($g = 2.0060$, $A_N = 14.33$, $a_H = 8.5$) has been detected in the Co(III)-OEP-cyclohexene system by the "spin trapping" method using nitrosodurene, which the authors[84] attributed to the cyclohexene radical-cation. We may add that there are indications in the literature of the formation of complexes by metalloporphines with unsaturated hydrocarbons[19,38,50] and, as shown in relation to the cyclohexa-1,4-diene-Co-Pc system, the complex formation equilibrium constant ($K_{cyclohexadiene}$) increases after the introduction of electron-accepting substituents into the phthalocyanine ring[19] (Table 13).

Table 13. The catalytic activity of substituted Co-Pc in the cyclohexa-1,4-diene-nitrobenzene system at 240 °C and the equilibrium constants (litre mol^{-1}) for the complex formation reactions between the catalyst and reactants[151].

Catalyst	α, %	K_{TNB}	$K_{CH\text{-}diene}$
Co-Pc	14	586	2.1
Co-Pc(F)$_4$	5	36	8.5
Co-Pc(F)$_{16}$	71	0.295	45

Notation: α = yield of benzene; K_{TNB} and $K_{CH\text{-}diene}$ are the equilibrium constants for the complex formation reactions of the catalyst with trinitrobenzene and cyclohexadiene respectively.

An acceptor mechanism of the catalysis has also been demonstrated for the oxidation reactions of thiols in an alkaline medium[52–58,62–66]. The catalysis of these reactions[54,57,58] consists of the coordination of the RS^- anion to M–Pc, the alternate reduction of M(II)-Pc by the thiol and the oxidation of the resulting M(I)-Pc by oxygen:

$$RSH + OH^- \rightarrow RS^- + H_2O ,$$
$$M(II)\text{-}Pc + RS^- \rightarrow M(I)\text{-}Pc + RS^{\cdot} ,$$
$$4M(I)\text{-}Pc + O_2 + 4H^+ \rightarrow 4M(II)\text{-}Pc + 2H_2O ,$$
$$2RS^{\cdot} \rightarrow RSSR .$$

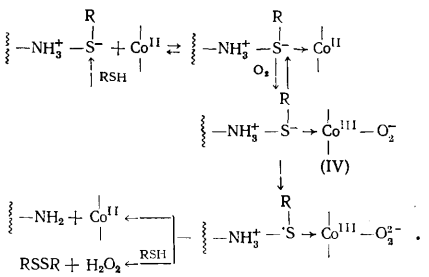
It has been shown by spectroscopy in the visible region[54] that in a phosphate buffer (pH 8.5–10.0) cysteine reduces the tetrasodium salt of cobalt(II)-4,4,4,4-tetrasulphophthalocyanine [Co(II)-Pc(SO_3Na)$_4$] to Co(I)-Pc(SO_3Na)$_4$. Subsequent introduction of oxygen into the system leads to a spectrum similar to that of Co(II)-Pc(SO_3Na)$_4$ when the reaction product is cysteine. Apparently Co(II)-Pc(SO_3Na)$_4$ forms a complex with cysteine.

The rate of oxidation of thiols usually depends on the M-Pc and O_2 concentrations but is independent of the thiol concentration[58], which shows that the thiolate anion reacts in the coordinated state. However, according to Kundo et al.[53], the rate of oxidation of cysteine is proportional to the cysteine and catalyst concentrations. Such conflicting data may be due to the difference between the ratios of the concentrations of the reactants used in different studies.

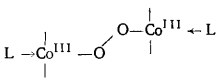
The coordination of the RS^- anion to the M-Pc during the reaction is also indicated by the decrease of the rate (up to the cessation of the reaction) caused by the addition of a strong complex-forming agent (the cyanide ion) in the oxidation of cysteine[57] and ethanethiol[58].

Effective catalysts have been proposed recently for the oxidation of thiols, the catalysts containing oxidation centres and basic groups involved in a cooperative interaction[62-66]. Such bifunctional catalysts consist of Co(II)-Pc(SO_3Na)$_4$ and a polymeric base (for example polyvinylamine or polyacrylamide modified by amino-groups) and exhibit a higher activity in the oxidation of 2-mercaptoethanol than the NaOH/Co(II)-Pc(SO_3Na)$_4$ low-molecular-weight system.

It has been suggested that RSH forms a complex with the polymeric base. The thiolate ion in this complex, which is a powerful π-donor, forms a complex with Co(II)-Pc(SO_3Na)$_4$, which coordinates an oxygen molecule, whereupon an electron is transferred within the coordination sphere from RS^- to O_2:[63]



The higher catalytic activity of polymeric catalytic systems compared with low-molecular-weight systems is associated with the fact that in the former case the very reactive mononuclear superoxo-complex (IV) is the effective species, while in the latter case dimerisation results in the formation of the less reactive dimericperoxo-complex (V):



(V)

Thus metalloporhines can catalyse oxidation-reduction reactions via two alternative mechanisms. The alteration of the electron-donating and electron-accepting properties of metalloporphines by the introduction of the appropriate substituents in the porphine ring can lead to the inversion of the mechanism of the catalysis in the same system. A similar phenomenon has been observed in the gas-phase oxidative dehydrogenation of cyclohexa-1,4-diene by nitrobenzene[151]. The metallophthalocyanines M-Pc catalyse this reaction by activating the oxidant, which is indicated by a series of facts—in particular by the increase of catalytic activity with decrease of the oxidation potentials of M-Pc (M = Mn, Fe, Co, Ni, Cu, or Zn) and with increase of the constants for their complex-formation reaction with trinitrobenzene. The enhancement of the electron-accepting properties of Co-Pc by the introduction of 16 fluorine atoms into its molecule changes the mechanism of the catalysis (Table 13). Depending on the number of fluorine atoms (from 0 to 16) in the phthalocyanine ring, the catalytic activity passes through a minimum; the oxidative dehydrogenation of cyclohexadiene in the presence of Co-Pc($F)_{16}$ takes place also in the absence of nitrobenzene; with increase of the number of fluorine atoms in the catalyst molecule, the constant for its complex formation reaction with trinitrobenzene diminishes and that for the reaction with cyclohexadiene increases.

IV. CATALYSIS OF THE DECOMPOSITION OF HYDROPEROXIDES

The presence of a variable-valence metal ion in metalloporphines gives rise to the possibility of yet another mechanism of the catalysis. They can initiate the autoxidation chain, catalysing via the Haber—Weiss mechanism[152] the decomposition of the hydroperoxides present in the substrate as impurities:

$$ROOH + M^{n+} \rightarrow RO^{\cdot} + OH^- + M^{(n+1)+} ,$$
$$ROOH + M^{(n+1)+} \rightarrow RO_2^{\cdot} + H^+ + M^{n+} . \qquad (4)$$

This mechanism usually operates at elevated temperatures. According to a number of studies[32-36], it predominates in the liquid-phase oxidation of cumene and a number of other hydrocarbons in the presence of M-Pc at temperatures above 105 °C; below 100 °C, the M-Pc activate oxygen. A change in the mechanism of the catalysis in the range 100–105 °C is indicated by the break in the temperature variation of the rate constant represented by a plot of $\lg k$ against $1/T$ as well as the lack of constancy of the ratio of the hydroperoxide formed to the oxygen which has reacted, observed above 105 °C. According to the results of other investigators the M-Pc catalyse the decompostion of cumenyl hydroperoxide also at 60–100 °C.[41,42,153].

In systems involving the oxygen activation mechanism, there is a possibility of the parallel catalysis of the decomposition of the hydroperoxides formed in the course of the reaction.

The composition of the cumene oxidation products in the presence of M-Pc at 80 °C and the catalytic activity of M-Pc depend on the nature of the metal (Table 14). In the case of Mn-, Fe-, and Co-Pc, the main reaction products result from the decomposition of cumenyl hydroperoxide: carbinol and acetophenone; in the case of Cu-, Zn-, and Mg-Pc, cumenyl hydroperoxide is virtually the only product; in the presence of Ni-Pc, the main product is cumenyl hydroperoxide but a certain amount of carbinol and acetophenone is also formed.

Table 14. The compositions (%) of the products of the oxidation of cumene catalysed by M-Pc at 80 °C over a period of 10 h.[154]

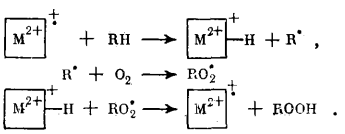
M	Mn	Fe	Co	Ni	Cu	Zn	Mg
Conversion of cumene	63.1	70.3	77.1	42.2	12.9	14.2	10.3
Hydroperoxide	17.9	12.4	5.8	31.7	12.9	14.2	10.3
Carbinol	31.8	40.8	50.0	9.0	0	0	0
Acetophenone	13.4	17.1	21.3	1.5	0	0	0
Selectivity with respect to hydroperoxide*	28.4	17.6	7.5	7.5	>98	>98	>98

* The content (%) of cumenyl hydroperoxide in the oxidation products.

The Mn-, Fe-, and Co-Pc catalysts are extremely active, since, together with the activation of oxygen, they also catalyse the decomposition of hydroperoxides; Cu-, Zn-, and Mg-Pc are capable of activating oxygen but do not catalyse the decomposition of hydroperoxides; Ni-Pc occupies an intermediate position—it is involved to some extent in reaction (4). These data can be interpreted from the

standpoint of the influence of the central metal on the mechanism of the oxidation of M-Pc (see Section II). The variable-valence metal ion necessary for the catalysis of the decomposition of hydroperoxides is present only in Mn-, Fe-, and Co-Pc, whose oxidation-reduction cycle proceeds via the central metal ion, and in Ni-Pc, whose oxidation-reduction takes place partly by the same mechanism; Cu- and Zn-Pc cannot catalyse the decomposition of hydroperoxides because their oxidation-reduction cycle proceeds only via the phthalocyanine ligand.

According to Manassen[155], the M-Pc whose oxidation involves a change in the valence of the metal ion catalyse the oxidation of cumene at elevated temperatures via the decomposition of the hydroperoxide, while the M-Pc whose oxidation proceeds via the ligand act as chain carriers:



Both mechanisms are possible for Ni-Pc.

V. CONCLUSION

The presence of an extensive π-conjugation system and of the central variable-valence metal ion in metalloporphine molecules gives rise to the possibility that they catalyse oxidation-reduction reactions via two alternative mechanisms: the donor mechanism, in which an electron is transferred in the course of the reaction from the catalyst to the oxidant, and the acceptor mechanism characterised by electron transfer from the substrate being oxidised to the catalyst molecule. The ratio of the oxidation-reduction potentials of the metalloporphine and the reactants of the reaction catalysed determines the mechanism of the catalysis in each specific system.

The presence of a variable-valence metal ion in the metalloporphine molecules also permits the initiation of the chain in the free-radical autoxidation by catalysing the decomposition of hydroperoxides via the Haber–Weiss mechanism.

Although porphyrin structures enter into the composition of oxidative enzymes and are active oxygen transferring agents in biological systems, synthetic metalloporphines catalyse under laboratory conditions as a rule the free-radical chain autoxidation. However, in certain systems the functioning of metalloporphines as agents transferring oxygen to the molecules of the substrate being oxidised is postulated. The search for such systems is of interest both from the standpoint of the elucidation of the mechanisms of enzyme catalysis and from the standpoint of the creation of new catalysts for the oxidation reaction which are selective as regards products.

We believe that studies in which the reaction is carried out in the presence of a suitable reductant, maintaining the catalyst in the reduced state, and the substrate being oxidised is activated with respect to nucleophilic attack by being coordinated to a suitable complex-forming agent merit attention. The employment of bimetallic porphyrin systems of the type obtained in a number of studies[156–161], one of the metallic centres of which (the donor) activates oxygen and the other (the acceptor) activates the substrate being oxidised, may also prove promising.

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Primary Photoprocesses in Colorant Molecules

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A survey is made of primary photoprocesses in dye molecules in solution—photophysical processes in excited singlet and triplet states (absorption from an excited level, vibrational and rotational relaxation, lifetimes, quantum efficiencies of fluorescence, intersystem and internal conversions, deactivation and quenching of the triplet state, etc.) and primary photochemical reactions (*cis-trans*-isomerisation, electron transfer, etc.). A list of 309 references is included.

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I. INTRODUCTION

Organic colorants are widely employed in various fields of science and technology—in the textile industry, colour and black-and-white photography, printing, etc.—absorbing light radiation efficiently and then transforming the resulting electronic excitation into various other forms of energy. Investigation of the interaction of intense light pulses with dye solutions led to the production of optical quantum generators having a tuned generation frequency (dye lasers). As traps for electronic excitation energy colorants can be used for the photostabilisation of polymeric materials. Finally, considerable interest has been aroused by study of the photosemiconductor properties of colorants with the aim of "sensitising" electrographic layers.

The development of experimental technique produced a substantial expansion of research on photoprocesses in colorant molecules. Laser sources enabled light pulses to be obtained of high intensity (~10^{13} W cm^{-2}) and short duration (10^{-9}–10^{-12} s). The use of such pulses to excite molecules made it possible to investigate primary photoprocesses lasting as little as 10^{-12} s.

Research on the photophysical and photochemical properties of organic dye molecules was last reviewed (1967) in a monograph[1]. Since then, an immense number of papers have appeared on the photonics of such molecules. The present Review covers the main results of research on primary photoprocesses in colorant molecules in solution published during the past decade.

II. PHOTOPHYSICAL PROCESSES IN MOLECULES IN A SINGLET EXCITED STATE

The processes occurring in colorant molecules in a singlet excited state (a lower excited state is implied) are extremely diverse. On absorption of a light quantum a molecule usually passes into upper vibrational sublevels of an electronically excited state. The processes following absorption include vibrational and rotational relaxation. The molecule can pass from the singlet excited state to the ground state with emission of a light quantum (fluorescence) or without emission (internal conversion), as well as to a triplet state (intersystem crossing) (Fig.1).

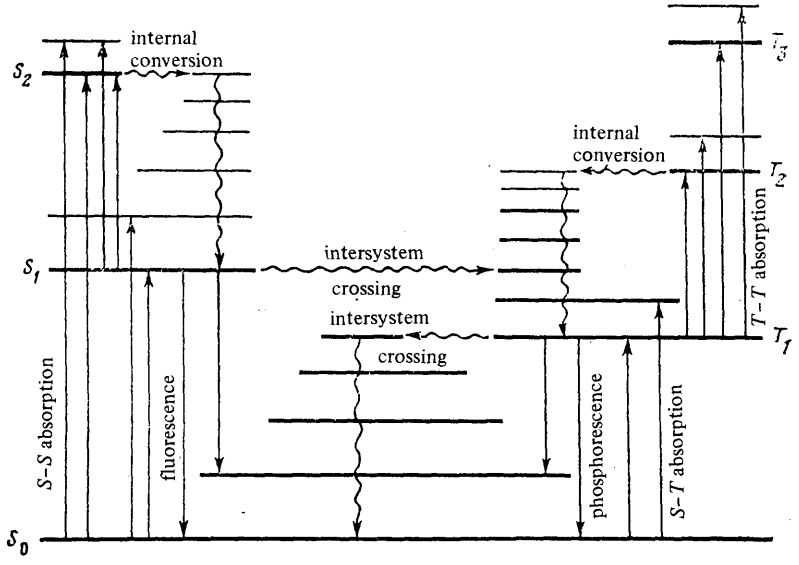


Figure 1. Scheme of energy levels in dye molecules and transitions between them.

Electromagnetic radiation of definite frequency induces forced transitions either to the ground state (amplification of light) or to a higher excited state (absorption of light). These unimolecular processes of deactivation of the singlet excited state may compete with bimolecular processes—energy or electron transfer—stimulated by transitions to ground and triplet states, formation of excimers and excited complexes, etc.

1. Singlet–Singlet Absorption

Absorption from a singlet excited level corresponds to $S_1 \rightarrow S_n$ transitions in the dye molecule (Fig.1). Their experimental investigation has been made possible during recent years by the development of picosecond laser spectroscopy. Spectra or effective $S_1 \rightarrow S_n$ absorption cross-sections have now been determined for several rhodamine[2–7] and cyanine[8–14] dyes, Cresyl Violet[15,16], Acridine Red[17], Nile Blue[6], etc.

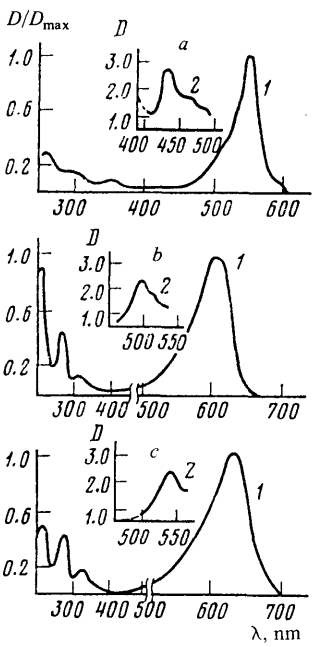


Figure 2. Absorption spectra[6] of ethanolic solutions of: *a*) Rhodamine 3B; *b*) Cresyl Violet; *c*) Nile Blue corresponding to the transitions: 1) $S_0 \rightarrow S_n$; 2) $S_1 \rightarrow S_n$. Optical densities D expressed in relative units.

Thus the $S_1 \rightarrow S_n$ absorption spectra of Rhodamines 6G and 3B in ethanol contain a maximum at 430 nm, but in that of Nile Blue the maximum occurs at 540 nm [6] (Fig.2). The corresponding spectrum of cryptocyanine has a band at 550 nm,[8,9] representing the energy difference between the S_2 and S_1 levels. For Cresyl Violet in methanol and in glycerol the maximum lies at 490–500 nm [6,15] and 430 nm [16] respectively. Here the energy of the $S_1 \rightarrow S_n$ transition does not correspond to any final state involved in absorption from the S_0 ground level. This was explained[15] by a symmetry difference between S_0 and S_1 states, which imposes restrictions on the probability of electron transitions. The absorption spectra of molecules in a singlet excited state give fresh information on the structure of the energy levels in colorant molecules.

2. Vibrational and Rotational Relaxation in a Singlet Excited State

Vibrational relaxation was first recorded in Rhodamine 6G by picosecond laser excitation[18]. The vibrational relaxation time was $\tau_{vibr} \cong 6$ ps, and a similar value 8 ± 3 ps was obtained later[19]; for Rhodamine B $\tau_{vibr} < 2$ ps. Subsequent studies have shown[20–24] that for these two colorants in ethanol, methanol, and water $\tau_{vibr} < 1$ ps, which is apparently the most reliable value.

The vibrational relaxation time for Rhodamine 6G dissolved in glycerol lengthens by only 50% over the temperature range 40–20 °C, while the viscosity increases more than thousandfold[25]. The lack of correlation between this time and the solvent viscosity indicates primarily that vibrational relaxation is due to interaction between solute and solvent molecules. In "isolated" molecules the time of "pure" vibrational relaxation is ~10^{-8} s.[26,27] A relation has been detected also with the quantum efficiency of fluorescence[25]: for Rhodamine B as example the quantum efficiency falls to 0.5 on passing from glycerol to ethanol, while the vibrational relaxation time shortens from 4 ± 1.4 to 0 ± 1.4 ps. The effect on the time was attributed to a difference in mobility of the terminal diethylamino-groups of the dye molecule in the two solvents[25]. An important part in the vibrational relaxation of rhodamines is played by hydrogen bonds between dye and solvent molecules. For the fluorescein group of xanthen colorants (fluorescein, eosin, erythrosin) $\tau_{vibr} < 10$ ps.[28]

The use of picosecond lasers has also enabled rotational or orientational relaxation in colorant molecules to be investigated[29–39]. Most of the measurements of rotational relaxation times have been made on Rhodamine 6G in various solvents. This time is directly proportional[29] to solvent viscosity (as follows from the Debye–Stokes–Einstein hydrodynamic model) and to hydrodynamic volume. Thus for Rhodamine 6G in ethanol the time τ_{rot} fluctuates from 70 to 300 ps according to various workers[29,33,34]. In viscous solvents it increases to 2800 ps [29,31] (or even to 6500 ps [32]) in undecanol and to 2100 ps in ethylene glycol[29,31]. Rotational relaxation times have been measured for Rhodamine 4S in ethanol (250 ps [38]), for Rose Bengal in several organic solvents varying in viscosity (in acetone and ethanol respectively 70 and 450 ps [37]), and for 3,3'-diethyloxadicarbocyanine (160 ps in ethanol[35]). Despite some divergence in the results, it can be accepted that, for the colorants investigated in low-viscosity media at room temperature, orientational equilibrium with the solvent is established before the act of emission.

3. Lifetime and Quantum Efficiency of Fluorescence

The lifetime of a singlet excited state τ_S^* is an important parameter determined by the aggregate of processes deactivating excited molecules. The use of picosecond lasers has enabled it to be found both from the decay of $S_1 \rightarrow S_n$ absorption intensity (for non-fluorescent molecules) and from the decay of fluorescence intensity. Such lifetimes have been measured for rhodamine[32,33,40–44,47,49], xanthen[28,32,41,54–57],

thiazine[58,129,149] azine[44,110], triphenylmethane[57,62,63], indigoid[54–67], coumarin[68,69], polymethine (cyanine)[13,35,70–84,110], and other colorants (Table 1).

Table 1. Lifetime τ_S^* and quantum efficiency ϕ_{fl} of fluorescence of dyes.

Dye	Solvent	τ_S^*, ns	φ_{fl}
Rhodamine 6G	methanol	3.7 [40]; 6.5 [41]	—
	ethanol	3.7 [33]; 4.5 [42, 44]	0.88 [42, 46]
	water	4.0 [44]	0.89 [46]; 0.96 [45]
	acetone	—	0.78 [46]
Rhodamine B	ethanol	3.4 [42]	0.81 [111]; 0.61 [42]; 0.72 [50]
	ethanol + HCl	2.5 [47]	0.49 [48]
	ethanol + KOH	3.1 [47]	0.71 [48]
Rhodamine 3B	ethanol	3.4 [42]	0.7 [111]; 0.68 [42]; 0.42 [46]
	water	—	0.37 [46]
NN'-Diethylrhodamine	ethanol	—	0.94 [42]
Fluorescein	ethanol	—	0.97 [54]
	water	4.0 [41]	—
	water (neutral dye)	—	0.14 [51]; 0.20—0.25 [52]
	water (monoanion)	—	0.26 [51]; 0.25—0.35 [52]
	water (dye cation)	—	0.9—1.0 [52]
	water, pH 9	—	0.92 [53]
	water, 0.05*N* NaOH	4.4 [32]; 3.9 [28]	—
Eosin	methanol	3.3 [54]	0.60 [54]
	ethanol	3.6 [54]	0.53 [111]; 0.69 [54]
	water, pH 7	0.90 [28]	0.19 [28]
	water, pH 9	—	0.19 [53]
	water, pH 9.2	1.4 [54]	0.20 [54]
Erythrosin	methanol	0.14 [55, 56]	0.08 [54]
	ethanol	0.56 [54]; 0.11 [28]	0.08 [54]; 0.02 [28]
	water	0.078 [57]	—
	acetone	2.4 [57]	—
Rose Bengal	methanol	0.66 [54]	0.08 [54]
	ethanol	0.82 [54]	0.11 [54]
	water, pH 9.2	0.095 [54]	0.018 [54]
Phenosafranine	ethanol	2.7 [44]	—
Methylene Blue	methanol	0.3 [58]	—
	water, pH 9	—	0.01 [59]
	water, pH 2.5	0.37 [149]	0.1 [60]
Thionine	water, pH 9	—	0.1 [60]
	water, pH 2.5	0.36 [129]	0.047 [129]
Acridine Orange	ethanol + 0.01M KOH	—	0.2 [61]
	water	1.7 [158]	—
Malachite Green	methanol	0.002 [63]	—
	glycerol	0.090 [57]; 0.010 [62]	—
	water, pH 9	—	0.01 [59]
Crystal Violet	ethanol	0.005 [62]	—
	glycerol	0.010 [62]	—
Thioindigo	toluene	13.0 [64]	—
	benzene	13.4 [66]	0.56 [66]
Indigo	benzene	<1 [67]	—
Coumarin 7	methanol	3.4 [68]	—
	ethanol	3.9 [68]	—
Coumarin 102	methanol	5.2 [68]	—
	ethanol	6.5 [68]	—
Coumarin 120	methanol	3.5 [69]	—
	ethanol	3.1 [69]	—
Pinacyanol (1,1'-diethyl-2,2'-carbocyanin	methanol	0.004 [71]	—
	ethanol	0.009 [71]	—
	glycerol	0.33 [70]	—
Cryptocyanine (1,1'-diethyl-4,4'-carbocyanine)	methanol	0.016 [76]	—
	ethanol	0.037 [71]; 0.080 [72]	0.017 [75]
	glycerol	0.075 [76]; 0.037 [77]	0.007 [77]
1,1'-Diethyl-2,2'-dicarbocyanine	methanol	0.007 [71]	—
	ethanol	0.011 [77]	0.003 [77]
	glycerol	0.145 [71]	—
3,3'-Diethyloxadicarbocyanine	ethanol	1.24 [80]; 1.2 [81, 84]	0.49 [80]; 0.42 [84]
	propan-2-ol	1.6 [35]	—
	water	0.56 [84]	—
3,3'-Diethyl-2,2'-thiatricarbocyanine	methanol	0.090 [13]	—

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

For rhodamine dyes in various solvents (water, methanol, ethanol, glycerol, etc.) the lifetimes lie in the range 2–6 ns. Variations are due to the experimental conditions. For example, τ_S^* falls from 4 to 2 ns with increase in the concentration of Rhodamine 6 G in water from 10^{-5} to 10^{-2} M,[41] which can be explained by singlet–singlet energy transfer from monomers to non-luminescing association complexes[40]. Lifetimes for rhodamine dyes became shorter on heating[85] owing to temperature quenching of fluorescence[86]. Later, however, it was concluded[87] that the excited singlet lifetime did not vary with temperature. Variation has been observed in the presence of detergents[88,89] and also with change in solution acidity[47,90].

Xanthen dyes of the fluorescein group have excited singlet lifetimes of the same order as those of the rhodamine group[28, 32,41,54], except for erythrosin and Rose Bengal, for which they are only around one-tenth[28,54–57]. Such a difference is due not only to the internal effect of the heavy atom[54] but also to a specific solvent effect. Thus these lifetimes for Rose Bengal in proton-donor solvents are some 20% of those in aprotic solvents[91], a difference attributed to the influence of hydrogen bonds on non-radiative transitions.

The shortest excited singlet lifetimes, a few picoseconds, are typical of triarylmethane dyes (Malachite Green, Crystal Violet)[62,63]. The decisive role in ultra-rapid electronic relaxation processes in such molecules belongs to internal conversion and conformational changes[16,63].

Brief lifetimes of singlet excited states have been found also in many polymethine dyes, apparently as a consequence of their capacity for *cis–trans*-photoisomerisation. The lifetimes increase in viscous media[70,71,78]. They depend on the length[92] of the polymethine chain $[CH:CH]_n$, changing approximately tenfold with increase in n from 1 to 3; further increase in n shortens the lifetime, to 50 ps for $n = 5$. The latter effect is explained by narrowing of the energy gap between S_0 and S_1 states and increase in the probability of non-radiative transitions.

An important characteristic of singlet excited states of molecules is the quantum efficiency of fluorescence ϕ_{fl}, which is determined from the singlet lifetime and the fluorescence rate constant k_{fl} by the formula $\phi_{fl} = k_{fl}\tau_S^*$.

Rhodamine dyes exhibit intense fluorescence, with quantum efficiencies exceeding 0.5 for most of them[42] (Table 1), which is explained by favourable relative positions of singlet and triplet energy levels[93]. The efficiency is affected by structural features of the rhodamine molecules[94] and also by such experimental conditions as the solvent[47,90], exciting wavelength[95,96], etc. It depends on the temperature: thus for Rhodamine B in alcohol the efficiency increases from 0.4 to 1.0 when the solution is cooled, and falls to a few percent on heating to 78 °C.[97]

The quantum efficiency ϕ_{fl} of the fluorescein group of xanthen dyes varies within wide limits as a consequence both of ionisation of the molecule (with change in solution pH) and of the effect of heavy atoms contained therein (Table 1). It is affected by hydrogen bonding between dye molecule and solvent[98], temperature[99], and deuteration[100].

For triarylmethane dyes the quantum efficiency of fluorescence is low ($\sim 10^{-4}$) in non-viscous media. However, it increases rapidly with the viscosity η, in conformity with the empirical relation $\phi_{fl} = c\eta^{2/3}$,[112] in which c is constant for a given dye.

Research on the spectral luminescent properties of cyanine dyes[75,77,80,84,101,102,110] has revealed a dependence of efficiency on the length of the polymethine chain analogous to the above relation for singlet lifetime[92]. The presence of *meso*-substituents in the chain usually lowers the efficiency. Introduction of a heavy atom into the heterocycle has little

effect[102]. Since polymethine dyes are capable of *cis–trans*-photoisomerisation, the effect of several factors on efficiency is in most cases a consequence of variation in the tendency to photoisomerisation.

Table 2. Quantum efficiencies of intersystem crossing and internal conversion ϕ_{is} and ϕ_{ic} and corresponding rate constants k_{is} and k_{ic} for dyes.

Dye	Solvent	φ_{is}	k_{is}, s^{-1}	φ_{ic}	k_{ic}, s^{-1}
Rhodamine 6G	ethanol	$2\cdot10^{-3}$ [114]; $5.5\cdot10^{-4}$ [111] *	$6.5\cdot10^{6}$ [42]; $1.6\cdot10^{6}$ [113] $4.2\cdot10^{5}$ [114]; $3.2\cdot10^{6}$ [115] $1\cdot10^{5}$ [111, 117] * $6\cdot10^{5}$ [116]	0.17 [119, 120]	$3\,1\cdot10^{7}$ [119, 120]
	methanol	—	$3.4\cdot10^{6}$ [118]	—	—
	bromoform + butanol (1 : 3)	0.12 [119]	$2.2\cdot10^{7}$ [119]	0.08 [119]	$1{,}4\cdot10^{7}$ [119]
	propanol	$3\cdot10^{-3}$ [121]	—	—	—
	water	$8\cdot10^{-3}$ [125]	—	—	—
	water, pH 1.4	$4\cdot10^{-4}$ [122]	—	—	—
	water, pH 5.2	$3\cdot10^{-3}$ [122]	—	—	—
	water, pH 7	$2\cdot10^{-3}$ [123,124]	—	—	—
Rhodamine B	ethanol + HCl	—	—	—	$9{,}7\cdot10^{7}$ [47]
	ethanol + KOH	—	—	—	$2{,}06\cdot10^{8}$ [47]
	ethanol	$3\cdot10^{-3}$ [111] *	$2.8\cdot10^{6}$ [115]; $6.7\cdot10^{5}$ [111] *	0.39 [119]	$1{,}1\cdot10^{8}$ [119]
	water	$6\cdot10^{-3}$ [123]	—	—	—
Rhodamine 3B	ethanol	$3.5\cdot10^{-3}$ [111] *	$1\cdot10^{6}$ [111] *	0.32 [119]	$9{,}4\cdot10^{7}$ [119]
NN'-Diethyl-rhodamine	ethanol	$1.5\cdot10^{-3}$ [111] *	$3.3\cdot10^{5}$ [111] *	0.06 [119]	$1{,}3\cdot10^{7}$ [119]
Fluorescein	water, pH 9	0.07 [53]	—	0.05 [98]	$1{,}4\cdot10^{7}$ [98]
	water, pH 7.2	0.02 [60]	—	—	—
	ethanol + 0.1M KOH	0.035 [61]	—	0.00 [61]	—
Eosin	water, pH 9	0.68 [53]	—	—	—
	water + 0.01M NaOH	0.76 [61]	$7.9\cdot10^{8}$ [118]	0.02 [61]	—
	ethanol	0.34 [126]	—	—	—
Erythrosin	water, pH 9	0.95 [53]	—	—	—
	ethanol	1.05 [60]; 1,0 [126]	—	—	—
Neutral Red	water, pH 9	<0.01 [59]	—	—	—
Methylene Blue	water, pH 9	0.54 [60, 127]	—	0.45—0.36 [59, 60, 127]	—
Thionine	water, pH 7.2	0.55 [60]	—	0.35 [60]	—
Acridine Orange	ethanol + 0.01M HCl	0.10 [61]	$6.8\cdot10^{7}$ [118]	0.44 [61]	—
	ethanol + 0.01M KOH	0.37 [61]; 0.30 [128]	—	0.43 [61]	—
Pinacyanol	methanol	$2.9\cdot10^{-3}$ [130]	—	—	—
	glycerol	$1.1\cdot10^{-2}$ [130]	—	—	$5.1\cdot10^{8}$ [71]
Cryptocyanine	ethanol	$6.3\cdot10^{-4}$ [77]	—	—	—
	glycerol	—	—	—	$6.9\cdot10^{8}$ [71]
1,1'-Diethyl-2,2'-dicarbocyanine	ethanol	$2.6\cdot10^{-4}$ [77]	—	—	—
	glycerol	—	—	—	$9.6\cdot10^{8}$ [71]
3,3'-Diethyl-oxadicarbocyanine	ethanol	$5\cdot10^{-3}$ [80]	—	0.43 [80]	—
3,3'-Diethyl-thiacarbocyanine	ethanol	$1\cdot10^{-2}$ [80]	—	0.52—0.64 [80]	—
	propanol	$1\cdot10^{-3}$ [131]	—	0.00—0.30 [131]	—

* At 77 K.

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

The fluorescence spectrum is characteristic of each dye. With almost all dyes the emission spectrum is located at the longer-wavelength edge of the principal absorption band. In addition to the usual fluorescence arising on transition from a lower singlet excited state to the ground state, a radiative transition from higher excited states is also possible, whose spectrum is displaced to shorter wavelengths (short-wave luminescence). The low quantum efficiencies and short lifetimes make detection of such luminescence difficult For dyes its observation therefore became possible after the creation of powerful laser sources of excitation. Short-wave luminescence has been investigated in solutions of Rhodamines 6G,[103–108], 3B,[109] and B,[104,109] cryptocyanine[78], etc. For these dyes it is characterised by low efficiencies $\phi_{fl} \cong 10^{-4}-10^{-6}$, while the excited states responsible for it are short-lived (~20–0.03 ps).

4. Intersystem Crossing and Internal Conversion

In the absence of processes tending to quench fluorescence and photochemical reactions involving a singlet excited state the non-radiative processes competing with fluorescence are intersystem crossing to a triplet state and internal conversion (Fig.1). Knowledge of quantum efficiencies or rate constants for these processes is necessary mainly because of the involvement of triplet states of colorants in various photoreactions. Methods elaborated for determining quantum efficiencies ϕ_{is} [59] have enabled values to be found for rhodamine[111,114,119,121–125], xanthen[53,60,61,126], thiazine[60,127], polymethine[77,80,110,131–134], and other dyes[59,61,128] in liquid solutions. Efficiencies ϕ_{is} together with rate constants $k_{is} = \phi_{is}\tau_S^{*-1}$ are listed in Table 2 for several dyes.

The efficiency ϕ_{is} of Rhodamine 6G has been determined from measurements of laser generation characteristics[135,136], triplet–triplet absorption[114,120–123,137], phosphorescence[111,117], and yields of photochemical reactions[138], but in several cases results obtained by different methods differed greatly. Those obtained from direct actinometric measurements[114] and by comparison with a standard[121–124] are apparently the most accurate (Table 2). Values of ϕ_{is} remain almost unchanged on passing from alcohol to water[114,123,124], but are appreciably lower in acid media (pH 1.4).[122] A significant increase is observed in media containing heavy atoms[119], as well as when the dye molecules are associated[120,139,140], in the latter case to 0.5. Both effects are due to strengthening of spin–orbit interaction.

The internal effect of a heavy atom in increasing the efficiency ϕ_{is} is especially clear in the series of xanthen dyes of the fluorescein group (Table 2). Thus passing from fluorescein to eosin (tetrabromofluorescein) and erythrosin (tetraiodofluorescein) increases the efficiency by factors of ~35 and ~50 respectively[60].

Low efficiencies $\phi_{is} \cong 10^{-2}-10^{-4}$ characterise many polymethine dyes in non-viscous solutions. Intersystem conversion to a triplet state has *cis–trans*-photoisomerisation as an effective competitor[131–134]. The quantum efficiency ϕ_{is} is significantly higher for dyes containing *meso*-substituents in the polymethine chain[131–134], because of steric hindrance to the competing process. An appreciable increase in efficiency has been observed in viscous media, in which *cis–trans*-isomerisation is likewise hindered[131].

Internal conversion competes with an intersystem transition to a triplet state. In the absence of photochemical reactions involving the singlet excited state the quantum efficiencies in the quenching of fluorescence conform to the relation

$$\varphi_{fl} + \varphi_{is} + \varphi_{ic} = 1 \qquad (1)$$

which enables the quantum efficiency of internal conversion ϕ_{ic} to be found from the observed efficiencies ϕ_{fl} and ϕ_{is}. Table 2 includes values of ϕ_{ic} and the rate constant of internal conversion k_{ic} for xanthen, thiazine, polymethine, and other dyes. It is evident that internal conversion is almost completely absent from fluorescein-group dyes in polar media:

an appreciable contribution by its efficiency has been observed only with fluorescein itself in dimethyl sulphoxide, dimethylformamide, and formamide[98]. The rate constant k_{ic} increases exponentially with decrease in the energy ΔE corresponding to the 0–0 band in the $S_0 \rightarrow S_1$ transition, which is governed by intermolecular interaction in the solute–solvent system[54,98]. Internal conversion is greater in rhodamine dyes, which also can be explained, apparently, in terms of the energetics of intermolecular hydrogen bonding[54].

Internal conversion makes a significant contribution to energy degradation of singlet excited molecules in the case of thiazine, acridine, triarylmethane, and polymethine dyes. It is especially effective in triarylmethane dyes, for which $\phi_{ic} \cong 1$, and $10^{-11}k_{ic}$ is respectively 5 and 2 s^{-1} for methanolic Malachite Green[63] and ethanolic Crystal Violet[62].

5. Quenching of Singlet Excited State

Dynamic quenching of fluorescence can occur mainly as a result of energy transfer, electron transfer, internal conversion or intersystem crossing under the influence of a quenching agent, formation of excimers and excited complexes, and other causes.

Quenching of singlet excited states of dye molecules by compounds having lower S_1 levels results from energy transfer by an inductive–resonance mechanism. Thus energy transfer has been established[141,142] between fluorescein and eosin, and correspondingly erythrosin and Rose Bengal. Picosecond laser technique has enabled such transfer to be investigated between Rhodamine 6G and 3,3'-diethylthiacarbocyanine[143], as well as Malachite Green[144–146]. For the Rhodamine 6G–Malachite Green system the critical energy-transfer radius $R_0 = 53$ Å and the transfer rate constant $k = 3.1 \times 10^{11}$ M^{-1} s^{-1}; for the Rhodamine 6G–3,3'-diethylrhodamine system in water $R_0 = 59$ Å. The efficiency of energy transfer is increased by the presence of a surface-active agent—sodium dodecyl sulphate[143].

Effective quenching of the fluorescence of dyes (Acridine Yellow, Magdala Red, phenosafranine, Rhoduline Red, etc.) by inductive–resonance energy transfer takes place in the presence of rare-earth metals (neodymium, erbium, praseodymium, etc.)[147,148]; the transfer radius is $R_0 = 10–13$ Å.

Many dyes undergo molecular association with increase in concentration[1]. Fluorescence quenching of monomeric dye molecules results from transfer of singlet excitation energy to non-luminescent association complexes. Detailed investigation of such concentration quenching has been made on rhodamine dyes[150–152].

Quenching of fluorescence accompanied by charge-transfer complex formation is assumed in the interaction of singlet excited rhodamine dye molecules with anthracene and its alkyl derivatives[153], as well as of xanthen dyes, Acridine Orange, and 7-hydroxycoumarin with oxygen[154]. Fluorescence quenching of Oxonine by allylthiourea increases the quantum efficiency of intersystem crossing to a triplet state[155], whereas that of Rhodamine 6G by diethylaniline makes internal conversion more probable[156]. Formation of a singlet excited complex is assumed in the fluorescence quenching of Pyronine by potassium iodide[157].

6. Effect of Association on Properties of Molecules in Singlet Excited State

With increase in concentration dyes may associate, which influences the properties of singlet excited states[1]. Thus raising the concentration of Acridine Orange to 0.1 M lengthens the singlet lifetime τ_S^* from 1.7×10^{-9} to 1.6×10^{-8} s.[158] For a pseudocyanine the formation of I-aggregates leads to shortening of this lifetime to 3.5×10^{-11} s, owing to migration of excitation energy within the aggregate[159]. Shortening of the lifetime has been observed also on the aggregation of rhodamine dyes[40,160].

Energy transfer by an inductive–resonance mechanism is possible for associated dye molecules. Such transfer has been observed between *NN'*-dioctadecyloxacyanine and *NN'*-dioctadecylthiacyanine[161]. Formation of excimers has been recorded also for polymethine dyes[162,163].

III. PHOTOPHYSICAL PROCESSES IN MOLECULES IN A TRIPLET STATE

Triplet states of dye molecules have an important role in the degradation of electronic excitation energy and are involved in various photochemical reactions. Triplet–triplet energy transfer is often used to populate the triplet level of molecules having low intersystem quantum efficiencies. Molecules in a triplet state have significantly longer lifetimes than singlet excited dye molecules, so that their spectra can be recorded by flash photoexcitation[164]. Triplet states of dyes are detected also from phosphorescence[1,111,165] and electron spin resonance[165–171] spectra.

1. Triplet–Triplet Absorption

Triplet–triplet (T–T) absorption corresponds to permitted transitions between triplet states (Fig. 1). Early work on flash photolysis involved detailed examination of T–T absorption spectra of xanthen dyes of the fluorescein group[172]. During recent years great interest has been taken in triplet states of rhodamine dyes in view of their widespread use in laser technique. The first direct determinations[137] of the corresponding spectrum of Rhodamine 6G with sensitised occupation of the triplet level of the dye molecules in butanol were soon confirmed[120,173]. The spectra of this dye in aqueous and alcoholic solution have been obtained by direct flash photoexcitation[114,116,122–124,140,174]. The T–T absorption band at 600–620 nm, where the laser emission by Rhodamine 6G is located, is accompanied by two additional T–T absorption bands, in the blue and in the infrared (Fig. 3).

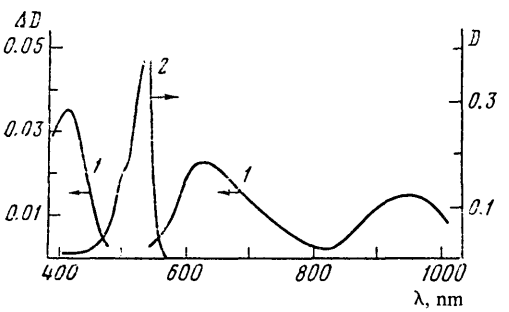


Figure 3. Absorption spectra[123] of aqueous Rhodamine 6G corresponding to the transitions: 1) $T_1 \rightarrow T_n$; 2) $S_0 \rightarrow S_n$.

The triplet–triplet absorption spectra of polymethine dyes have been investigated in detail in connection with their use as active media for optical lasers[11,130,131,133,175–181]. Because

of the low intersystem quantum efficiencies the spectra were obtained for most of these dyes with sensitised excitation. Such spectra have been determined for thiazine dyes (Thionine[182–185], Methylene Blue[186–190], Methylene Green[187]), acridine dyes (Acridine Orange, Acridine Yellow)[191–194], indigoid dyes (thioindigo, 6,6′-diethoxythioindigo)[195,196], coumarin dyes (coumarin, 7-hydroxycoumarin, 7-diethylamino-4-methylcoumarin)[197–199], and other dyes.

2. Deactivation of Triplet States

In photoreactions of dyes the quantum yield of the primary product is directly proportional to the lifetime of the molecule in any triplet state involved. Hence knowledge of the characteristics of processes effecting deactivation of such triplet states is extremely important for assessing the efficiency of photochemical reactions.

A distinction must be made between uni- and bi-molecular deactivation processes. The former include phosphorescence, intersystem crossing, and thermally activated delayed fluorescence (delayed fluorescence of type *E*/200). Among the second are triplet–triplet annihilation fluorescence (delayed fluorescence of type *P*/200), concentration quenching, and electron transfer on disproportionation of two triplet molecules and on interaction of a triplet with an unexcited molecule, as well as deactivation of a triplet state by various quenching agents.

Unimolecular deactivation processes. The lifetime of a molecule in a triplet state is determined by the totality of deactivation processes. In the absence of triplet–triplet annihilation and of concentration and other quenching processes this lifetime is given by

$$\tau_T = (k_{ph} + k_e + k_0 + k_q[Q])^{-1}$$

which takes into account the unimolecular (pseudounimolecular) deactivation processes

$$T \xrightarrow{k_{ph}} S + h\nu_{ph} \qquad (2)$$

$$T \xrightarrow{k_e} S^* \qquad (3)$$

$$T \xrightarrow{k_0} S \qquad (4)$$

$$T + Q \xrightarrow{k_q} S + Q\ . \qquad (5)$$

In most cases phosphorescence (2) cannot be recorded in liquid dye solutions at room temperature, owing to rapid non-radiative deactivation of the triplet state (4) and (5). It has been recorded in solutions of rhodamine dyes in the presence of bromoform (20–30 vol.%), which facilitates transition to a triplet state[209,212,229], the quantum efficiency of phosphorescence being (2–6) × 10^{-5}.[209] Systematic measurements of phosphorescence have been made for xanthen dyes at 77 K.[203,208,230] The longest triplet lifetimes occur in solid matrices—solutions at low temperatures or films (e.g. polyvinyl alcohol)—and are determined from the kinetics of the decay of phosphorescence[203,208], triplet–triplet absorption[198], and the e.s.r. signal[166,169,202,231,232]. Values of τ_T for most colorants under these conditions lie in the range 0.1–1.0 s (Table 3).

Several colorants (e.g. xanthen dyes) exhibit delayed fluorescence of type *E*. This process (3) involves vibrational excitation of T_1 to an isoenergetic level S_1 followed by an intersystem transition at S_1 and loss of excitation by fluorescence (Fig.1). Delayed fluorescence of this type is observed with compounds having small singlet–triplet separation (2000–3000 cm^{-1}), as well as at high temperatures.

Table 3. Lifetime τ_T and deactivation rate constants of triplet state of dyes.

Dye	Solvent	τ_T, s	k_0, s^{-1}	k_1, s^{-1}	$2k_{TT}$, M^{-1}	k_{TS}, s^{-1}	Ref.
Fluorescein	water, pH 12	—	—	5·10	$1.7\cdot10^9$	$1\cdot10^8$	[59]
	polyvinyl alcohol (pva)	—	7.6	—	—	—	[59]
	ethanol (77 K)	0.18	—	—	—	—	[202]
Eosin	water, pH 9.1	—	—	$5.4\cdot10^2$;	$1.1\cdot10^9$	$3\cdot10^8$	[59]
	water, pH 9.1	—	—	$4.2\cdot10^2$	—	$4\cdot10^8$	[204]
	pva	—	$2.3\cdot10^2$	—	—	—	[59]
	ethanol (77 K)	0.10	—	—	—	—	[202]
	water, pH 7.0	—	—	$4.06\cdot10^2$	—	—	[205]
Erythrosin	water, pH 10	—	—	$3\cdot10^3$	—	—	[59]
	pva	—	$1.6\cdot10^3$	—	—	—	[59]
	water, pH 9.3	—	—	$5.2\cdot10^3$	—	$2.2\cdot10^8$	[204]
Rhodamine 6G	ethanol	—	—	10^3—10^4	$4.1\cdot10^9$	—	[114]
	ethanol (77 K)	1.7	—	—	—	—	[202]
	ethanol + O_2	$0.45\cdot10^{-6}$	—	—	—	—	[114]
		$0.33\cdot10^{-6}$					[115]
	butanol	—	—	$1.7\cdot10^2$	—	—	[210]
	butanol + 20% bromoform	—	—	$1.5\cdot10^3$	—	—	[120]
	propanol + 20% bromoform	—	5·10	—	—	—	[209]
	water, pH 6	—	$4\cdot10^4$*	$4\cdot10^2$	$2.8\cdot10^9$	$5\cdot10^7$	[140]
Rhodamine B	butanol + 30% bromoform	—	—	$1.6\cdot10^3$	—	—	[119]
	ethanol (77 K)	1.0	—	—	—	—	[202]
	ethanol + O_2	$0.33\cdot10^{-6}$	—	—	—	—	[115]
	ethylene glycol (90 K)	0.86	—	—	—	—	[169]
Rhodamine 3B	butanol + 30% bromoform	—	—	$2.2\cdot10^3$	—	—	[119]
Thionine	methanol + 20% water (98 K)	$3.5\cdot10^{-3}$	—	—	—	—	[171]
	water, pH 1–8	—	—	$8.5\cdot10^4$	—	—	[215]
	water, pH 1.7	—	—	$1.5\cdot10^5$	—	—	[188]
	water, pH 2.5	$1.6\cdot10^{-5}$	—	—	—	—	[183]
Oxonine	methanol + 20% water (98 K)	$3\cdot10^{-2}$	—	—	—	—	[171]
	water	—	—	$8.3\cdot10^3$	—	—	[217]
Methylene Blue	methanol + 20% water (98 K)	$2\cdot10^{-3}$	—	—	—	—	[171]
	water	$(4\div6)\cdot10^{-5}$	—	$1.52\cdot10^4$**	—	—	[219]
	water, pH 5	—	—	$2.3\cdot10^5$	—	—	[190]
	water, pH 9	—	—	$1.2\cdot10^4$	—	—	[187]
				$0.3\cdot10^5$***	—	—	
	acetonitrile	—	—	$6.5\cdot10^3$	—	$9\cdot10^8$	[189]
Acridine Orange	methanol	—	—	$3.5\cdot10^3$	$5.5\cdot10^9$	—	[194]
	methanol + chloroacetic acid	—	—	—	$1.6\cdot10^9$	—	[194]
	water, pH 12	—	—	$3\cdot10^2$	$5.5\cdot10^9$	$3\cdot10^8$	[192]
	water + 10^{-3} M HCl						
	water, pH 2	—	—	$3\cdot10^2$	$4\cdot10^9$	$\sim10^8$	[228]
		—	—	$2.5\cdot10^3$	$1.5\cdot10^9$	$2.3\cdot10^7$	[221]
	ethanol (77 K)	2.0	—	—	—	—	[202]
	pva	—	11.5	—	—	—	[221]
Acridine Yellow	water, pH 11	—	—	$6\cdot10^2$	$3.1\cdot10^9$	$7.6\cdot10^8$	[221]
	water, pH 2	—	—	$1.9\cdot10^3$	$3.8\cdot10^9$	$2.0\cdot10^8$	[221]
	ethanol (77 K)	3.1	—	—	—	—	[202]
	pva	—	1.5–4.2	—	—	—	[221]
3,3′-Diethylthiadicarbocyanine	propanol	—	—	$2.3\cdot10^2$	$2.6\cdot10^9$	$4.0\cdot10^7$	[222]
	butanol	—	—	$4.6\cdot10^2$	—	—	[133]
	pva	—	$1.5\cdot10^2$	—	—	—	[223]
3,3′-Diethylthiadicarbocyanine	propanol	—	—	$3.0\cdot10^2$	$2.4\cdot10^9$	$1.3\cdot10^7$	[222]
				$5.4\cdot10^2$****			
	pva	—	$2.5\cdot10^2$	—	—	—	[223]
Cryptocyanine	ethanol	—	—	$9.1\cdot10^2$	—	—	[77]
	glycerol + O_2	$4\cdot10^{-5}$	—	—	—	—	[226]
Pinacyanol	methanol	—	—	$5.3\cdot10^3$	—	—	[130]
8,9-Difluorothiacarbocyanine	propanol + O_2	$4.2\cdot10^{-6}$	—	$9.3\cdot10^5$	—	—	[175]
3,3′-Diethyl-9-methoxythiacarbocyanine	Propanol	—	—	$4\cdot10^2$	$2\cdot10^9$	$1.9\cdot10^7$	[222]
7-Hydroxycoumarin	ether + isopentane + ethanol (5 : 5 : 2) (77 K)	0.90	—	—	—	—	[198]
	ditto (117 K)	0.10	—	—	—	—	[197]
Thioindigo	benzene	$1.35\cdot10^{-7}$;	—	—	—	—	[227]
	benzene	$2.79\cdot10^{-7}$	—	—	—	—	[196]

*Ref.116.
**Ref.218.
***Ref.190.
****Ref.224.

In deoxygenated liquid solutions the chief processes deactivating a triplet state are non-radiative degradation (4) and quenching by uncontrollable impurities (5). Table 3 lists rate constants k_0 and $k_1 = k_0 + k_Q[Q]$ for various classes of dyes, and Table 4 gives positions of the triplet level E_T for the molecules. Several conclusions follow from these data: (i) k_1 exceeds k_0 for all the compounds investigated (the difference between them is due mainly to quenching by residual oxygen, whose concentration is estimated as $(1-2) \times 10^{-7}$ M); (ii) k_0 and k_1 increase with the number of heavy atoms in xanthen dye molecules in the sequence—fluorescein < eosin < erythrosin—and also in polymethine dyes (internal heavy-atom effect)[102]; (iii) k_1 for the rhodamine group of xanthen dyes is greater in media containing heavy atoms, e.g. bromoform (external heavy-atom effect); (iv) protonation of thiazine and acridine dye molecules increases k_1, as a consequence of the position of the triplet level in protonated molecules; (v) the high values $k_1 \cong (2-3) \times 10^8$ s^{-1} for thioindigoid dyes are due to the involvement of the triplet state in photoisomerisation; and (vi) k_1 for triarylmethane dyes increases on passing from a solid matrix to a solution, as conformational changes and additional rotational modes become possible.

Table 4. Triplet levels E_T of dye molecules.

Dye	Solvent	E_T, cm^{-1}	Ref.
Fluorescein	*	16500	[201]
»	ethanol	18000	[203]
Eosin	ethanol	15600	[203]
»	*	15900	[206]
»	*	14800	[207]
Erythrosin	water, pH 9	14700	[213]
Rhodamine 6G	ethanol	15100	[203, 208]
»	propanol + 20% bromoform	14400	[209]
»	propan-2-ol	14650	[211]
»	propanol + 30% bromoform	14900	[212]
Rhodamine B	propanol + 20% bromoform	14300	[209]
»	ethanol	14890	[203]
Rhodamine 3B	ethanol	14870	[203]
Thionine	water + KOH	13700	[214]
»	water + HCl	10500	[214]
»	*	13900	[216]
Methylene Blue	water + KOH	11640	[220]
»	water + HCl	8220	[220]
Acridine Orange	*	17100	[111]
Acridine Yellow	*	18350	[111]
3,3′-Diethylthiacarbocyanine	propanol	13750	[225]
3,3′-Diethylthiadicarbocyanine	propanol	<12600	[225]

*Solvent not stated.

Triplet–triplet annihilation and concentration quenching. Bimolecular processes include triplet–triplet interaction (at high concentrations of triplet molecules) and concentration quenching. Provided that the singlet–triplet splitting in the molecule is less than the separation between triplet and ground levels, excitation energy can be transferred between two triplet molecules with transition of one of them to a singlet excited state followed by fluorescence (delayed fluorescence of type *P*). Other possible results of triplet–triplet interaction may be non-radiative degradation[200, 233] and electron transfer[59,234]:

$$T + T \xrightarrow{k_{TT}} \begin{cases} \rightarrow S^{*} + S & (6) \\ \rightarrow \tilde{S} + S & (7) \\ \rightarrow R^{+} + R^{-} \cdot & (8) \end{cases}$$

The triplet–triplet interaction rate constant k_{TT} is usually found from the rate of decay of triplet–triplet absorption intensity. Table 3 gives values of k_{TT} for individual xanthen, acridine, and polymethine dyes; high values indicate that triplet–triplet interaction is occurring in the diffusion range.

Delayed fluorescence of type *P*, resulting from triplet–triplet annihilation, is observed in liquid dye solutions. That of butanolic Rhodamine 6G in the presence of bromoform[229] is assumed to involve formation of a ternary complex of two triplet dye molecules and one bromoform molecule. With photoexcitation sensitised by triplet–triplet energy transfer account must be taken also of delayed fluorescence due to triplet–triplet annihilation of mixed type[224,235].

Concentration quenching of triplet states arises from interaction of a triplet with an unexcited molecule. Its mechanism has not been finally established, but it apparently results from formation of a vibrationally excited molecule in the ground state[236], excimer phosphorescence[59], and electron transfer[59,172,234]:

$$T + S \xrightarrow{k_{TS}} \begin{cases} \rightarrow \tilde{S} + S & (9) \\ \rightarrow [T_2] \rightarrow S + S + h\nu & (10) \\ \rightarrow R^{+} + R^{-} & (11) \end{cases}$$

Table 3 includes concentration-quenching rate constants k_{TS} for several dyes. Comparison of k_{TS} and k_{TT} indicates that concentration quenching is substantially less effective than triplet–triplet interaction.

3. Quenching of the Triplet State

A distinction is made between static and dynamic quenching of triplet states. The former involves a decrease in concentration of triplet molecules unaccompanied by change in their lifetime. Static quenching corresponds to equilibrium between molecules unperturbed by the quenching agent and those that have been affected by the quencher (complex formation with the latter, association, etc.) and have a lower intersystem quantum efficiency ϕ_{is}. Dynamic quenching of the triplet state occurs in encounters of triplet with quencher molecules and shortens their lifetime.

A distinction is made also between "physical" and "chemical" quenching: the former yields the initial molecules in a ground (vibrationally excited) or an electronically excited state, but the latter gives intermediate products, e.g. free radicals. Physical quenching includes triplet–triplet interaction, concentration quenching, and quenching by heavy atoms; quenching by electron donors and acceptors, etc. must be regarded as chemical.

The chief processes for quenching the triplet state of dye molecules are triplet–triplet energy transfer, electron transfer, quenching by an "external" heavy-atom mechanism, and paramagnetic quenching.

Triplet–triplet energy transfer is one way in which the triplet state of a donor is quenched by an energy acceptor[233, 237]. Measurements of such transfer have revealed that the rate constant depends on the separation ΔE_T between the triplet levels of donor and acceptor. With large $\Delta E_T \geq 1500$ cm^{-1} the rate constant remains almost unchanged, close

to the diffusion constant; with decrease in the separation the rate constant k_q decreases; and with $\Delta E_T < 0$ there is a linear dependence of $\ln k_q$ on ΔE_T.[238,239]

Table 5. Triplet–triplet energy-transfer quenching rate constants for dyes.

Dye	Quencher	Solvent	k_q, M^{-1} s^{-1}	Ref.
Fluorescein	O_2	water, pH 12	$1.6 \cdot 10^9$	[204]
Eosin	O_2	water, pH 8.6	$1.1 \cdot 10^9$	[204]
»	O_2	water	$(1.1–2.0) \cdot 10^9$	[240]
»	Cu^{2+}	water, pH 6.2	$5.6 \cdot 10^8$	[255]
»	anthracene	ethanol	$5.1 \cdot 10^8$	[207]
Erythrosin	anthracene	ethanol	$7.3 \cdot 10^8$	[207]
Rhodamine 6G	O_2	ethanol	$2.5 \cdot 10^8$	[241]
»	O_2	ethanol	$1.6 \cdot 10^9$	[114]
»	O_2	methanol	$3.3 \cdot 10^9$	[242]
»	O_2	water	$6 \cdot 10^8$	[116]
»	cyclo-octatetraene	ethanol	$7.0 \cdot 10^8$	[114]
»	Co^{2+}	water	$2.6 \cdot 10^7$	[124]
Thionine	O_2	water, pH 4.6	$2.6 \cdot 10^8$	[215]
»	O_2	water, pH 8	$4.5 \cdot 10^8$	[183]
»	Co^{2+}	water, pH 2.5	$5 \cdot 10^5$	[243]
Methylene Blue	O_2	water	$3 \cdot 10^9$	[219]
3,3′-Diethylthiacarbocyanine	naphthacene	butanol	$1 \cdot 10^9$	[180]
3,3′-Diethyl-9-methoxythiacarbocyanine	naphthacene	propanol	$3.7 \cdot 10^9$	[134]

Table 6. Rate constants k_q for quenching of the triplet state of dyes by compounds containing heavy atoms.

Dye	Solvent	Quencher	k_q, M^{-1} s^{-1}	Ref.
Rhodamine 6G	ethanol	KI	$2 \cdot 10^9$	[244]
»	ethanol	KI	$1.1 \cdot 10^9$	[115]
»	propanol	LiBr	$5 \cdot 10^3$	[212]
»	propanol	CBr_4	$4.6 \cdot 10^4$	[212]
»	propanol	$CHBr_3$	$2 \cdot 10^2$	[212]
Rhodamine B	ethanol	KI	$2.2 \cdot 10^8$	[115]
Eosin	water, pH 6.5	KI	$1.5 \cdot 10^7$	[245]
»	water, pH 6.2	KI	$1.5 \cdot 10^7$	[246]
»	water, pH 7.1	KI	$1.9 \cdot 10^7$	[247]
»	water	$HgCl_2$	$5 \cdot 10^8$	[219]
»	water	TlCl	$2 \cdot 10^7$	[219]
»	water	CsCl	10^5	[219]
Thionine	methanol	C_6H_5Br	$4 \cdot 10^4$	[248]
»	water, pH 7.1	KI	$4.7 \cdot 10^9$	[247]
Methylene Blue	water	KI	$1 \cdot 10^7$	[219]
»	water	CsCl	$2 \cdot 10^6$	[219]
»	water	$HgCl_2$	$2 \cdot 10^9$	[219]
»	water	TlCl	$2 \cdot 10^8$	[219]
Safranine T	water, pH 9	KI	$1 \cdot 10^8$	[59]
3,3′-Diethyl-9-methoxythiacarbocyanine	butanol	$CHBr_3$	$2.5 \cdot 10^5$	[134]

Energy acceptors in the quenching of triplet states of dyes include oxygen molecules, aromatic hydrocarbon molecules, and inorganic ions. Quenching by oxygen has been studied in the greatest detail: it is generally accepted that quenching results in the formation of singlet oxygen[237], but electron transfer is also possible[204,249]. Table 5 gives triplet-quenching rate constants for various energy acceptors.

Compounds containing heavy atoms (bromobenzene, bromoform, alkali-metal bromides and iodides, hetero-organic compounds of tin, lead, mercury, etc.) facilitate intersystem transitions and lead to triplet quenching in both liquid and solid solutions[59]. Those in Table 6 can be arbitrarily divided into two groups according as k_q lies in the ranges 10^2–10^5 and 10^7–10^9 M^{-1} s^{-1}. Differences in the values of k_q are due to different quenching mechanisms: weak quenching (by bromoform, bromobenzene, caesium chloride, lithium bromide) is caused by direct spin–orbit interaction, but effective quenching by potassium iodide and by mercury(II) and thallium(I) chlorides involves electron transfer.

4. Triplet States of Association Complexes

At high dye concentrations association complexes are formed in polar solvents, in micellar solutions by interaction with macromolecular compounds, and also in mixtures of a polar and a non-polar solvent[1]. Association is accompanied by change in the spectral luminescent properties of the molecules.

Triplet states of association complexes have been investigated mainly on the rhodamine group of xanthen dyes[120,140,210,250–254]. Association of Rhodamine 6G in tetrachloromethane, cyclohexane, benzene, etc. in the presence of 0.1–0.2% of a polar solvent (association complexes of type I), as well as in aqueous solution in the presence of polymethacrylic acid (association complexes of type II) increases significantly the quantum efficiency of intersystem crossing in the triplet state relative to that of the dye monomers (ϕ_T respectively ~0.2 and ~0.5 for types I and II). The quantum efficiency of internal conversion also increases, and that of fluorescence decreases. The increase in ϕ_T accompanying association of Rhodamine 6G may be due to strengthening of spin–orbit interaction on aggregation and narrowing of singlet–triplet separation[252].

The triplet state of associated Rhodamine 6G is deactivated in uni- and bi-molecular processes. In 0.2% butanol–99.8% tetrachloromethane mixtures both delayed fluorescence of type *E* and phosphorescence are observed[250,251]. Measurements of the lifetime of the triplet state have shown that the deactivation rate constant k_1 increases from 200 to 3000 s^{-1} on passing from type II to type I association complexes[254]. The longer lifetime for the former is probably due to stabilisation of the complexes by the polymer. An analogous stabilising effect of polymethacrylic acid has been found for monomeric Rhodamine 6G.[140] The rate constant k_1 depends on the nature of the polar component of the mixture (viscosity and capacity for hydrogen bonding)[140,254]. Associated Rhodamine 6G can undergo triplet concentration quenching and triplet–triplet interaction[254], the latter accompanied by delayed fluorescence of type *P*.[210]

Many dyes are ionic compounds[1]. At certain solution concentrations charged dye ions are able to form ionic association complexes with a gegenion. Photophysical processes have been investigated in ionic association complexes of xanthen dyes of the fluorescein series with transition and rare-earth metal ions[256–261]. The measured phosphorescence lifetimes of the dye complexes with rare-earth metal ions in ethanol at 77 K indicate transfer of the triplet excitation energy to the metal ion. Sensitised luminescence of the trebly charged ytterbium cation has been detected in associated dyes in liquid solutions. The nature of the gegenion influences the relative quantum efficiencies of fluorescence and phosphorescence in the association complexes: thus the phosphorescence of eosin completely vanishes in complexes with the ytterbium(III) cation, whereas its quantum efficiency increases in the presence of trebly charged europium, gadolinium, terbium, and cerium cations.

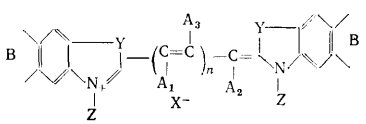
IV. PRIMARY PHOTOCHEMICAL REACTIONS OF DYES

Dyes undergo various photochemical reactions in solutions[1]. Primary photochemical processes can occur at any stage in degradation of the energy of singlet and triplet excitation.

Three types of reaction can be distinguished, independently of the multiplicity of the excited state[262]: reactions of type A take place in a vibronic state immediately after absorption of a light quantum, those of type B follow vibrational relaxation, and type C occur after transition to a vibrationally excited level of the ground state, or to a triplet state. Type A reactions, proceeding from an unrelaxed vibrationally excited state, should have rate constants exceeding 10^{11}–10^{13} s^{-1}; they include photodissociation and photoisomerisation. Such reactions are unimolecular, with kinetics depending on temperature and exciting wavelength. Type B—electron, proton, etc. transfer—are of great interest for the photochemistry of dyes. The main factors influencing the reactivity of molecules are energy, multiplicity, distribution of electron density, and orbital symmetry.

1. *cis–trans*-Photoisomerisation

cis–trans-Photoisomerisation has been studied in greatest detail on cyanine (polymethine) dyes of structure



Y=O, S, $C(CH_3)_2$; Z=CH_3, C_2H_5; A_1, A_2=H, CH_3, F; A_3=H, F, CH_3, C_2H_5, OCH_3, NH_2; n = 0, 1, 2, 3; B = H, 5-NO_2, 5-H_2CO, 6-$N(CH_3)_2$, 6-Br, 6-NH_2OH, OCH_3, I, NO_2; X=I, CH_3SO_4, Br, ClO_4

It has been investigated in solid matrices[265] and in liquid solutions with flash (microsecond)[130–132,134,175,180,263,264,268,270] and laser (nanosecond[266,267,269,273–276] and picosecond[176,271,272]) excitation.

In the ground state polymethine dye molecules may occur in either the *trans* or the *cis* form. Photoexcitation may correspondingly involve *trans* → *cis* or *cis* → *trans* transitions. Thus 3,3'-diethylthiacarbocyanine, which has an unsubstituted polymethine chain, on excitation passes from the *trans* into the *cis* form[264]. *trans–cis*-Isomerisation takes place about the $C_{(2)}$–$C_{(8)}$ bond in the unsubstituted and 10-substituted polymethine chain, and about the $C_{(8)}$–$C_{(9)}$ bond in *meso*-substituted dyes[270].

cis–trans-Photoisomerisation of polymethine dyes takes place in the singlet state S_1,[266,277] as indicated primarily by triplet–triplet energy transfer results. Sensitised population of the triplet level of these dyes gives a triplet–triplet absorption spectrum markedly different from that of the photoisomers[130,131,134,175,180,264,269,273]. Furthermore, the fluorescence of 3,3'-diethylthiacarbocyanine decays and its *cis*-isomer accumulates within the same time (300 ps).[272] However, *cis–trans*-photoisomerisation from the triplet state is possible with 8,9-difluorothiacarbocyanine[274].

On excitation in the $S_0 \rightarrow S_n$ transition band, isomerisation follows internal conversion $S_n \rightarrow \tilde{S}_1$ and vibrational relaxation $\tilde{S}_1 \rightarrow S_1$.[267,278] However, picosecond laser excitation enabled isomerisation to be recorded in the S_2 state of 3,3'-diethyl-2,2'-thiacarbocyanine[12]. The rate constant in methanol is 3.2×10^{10} s^{-1}, which ensures that isomerisation can compete successfully with internal conversion ($k_{ic} = 1.8 \times 10^{10}$ s^{-1}).

Fig. 4 shows the transitions in substituted thiacarbocyanines when the initial form is a *cis*-isomer. The absorption and fluorescence spectra of isomers usually differ insignificantly, with shifts of 5–20 nm. Extinction coefficients are also closely similar[176,266,272].

Polymethine dyes are usually characterised by high quantum efficiencies of photoisomerisation ϕ_{isom}. Table 7 lists quantum efficiencies ϕ_{fl}, ϕ_{is}, and ϕ_{isom}, rate constants of triplet deactivation k_1 and relaxation of the photoisomer k_{relax}, and also activation energies of relaxation E_a for 3,3'-diethylthiacarbocyanine and its substituted derivatives. It is evident that non-radiative degradation of the energy of singlet excited states is effected mainly by isomerisation with characteristics (ϕ_{isom}, k_{relax}, E_a) depending on the presence in the polymethine chain of substituents capable of offering steric hindrance to rotation on isomerisation. Replacement of one hydrogen atom at position 8 or 9 by a fluorine atom does not produce significant steric hindrance, so that long-lived photoisomers are formed (lifetime 10^{-3}–10^{-2} s) with an angle of rotation of the chain $\alpha = 180°$. Replacing two or three hydrogen atoms leads to marked steric hindrance, with the angle decreasing to 90°, the photoisomer relaxation rate constant increasing abruptly, and the activation energy of relaxation simultaneously diminishing. Analysis of Stuart–Briegleb models shows that similar changes in k_{relax}, E_a, and α always accompany steric hindrance[273]. If such hindrance is sufficiently great, photoisomerisation may be completely suppressed[279].

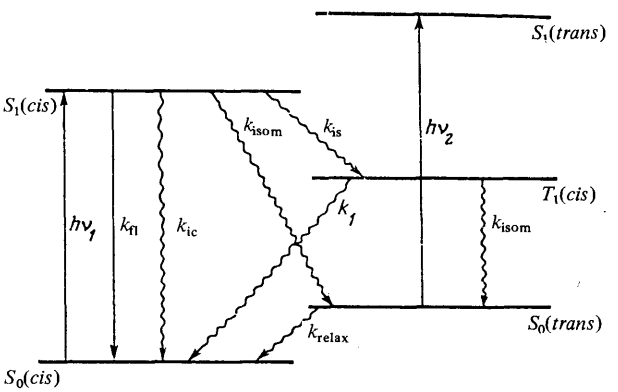


Figure 4. Scheme of energy levels and transitions between them for *cis*- and *trans*-isomers of thiacarbocyanines.

Replacement of hydrogen atoms in polymethine dyes by halogens leads to a redistribution of probabilities of singlet deactivation of excited states as a consequence not only of steric hindrance but also of an internal heavy-atom effect. Thus for 9-iodothiacarbocyanine $\phi_{is} = 1$ but $\phi_{isom} \cong 0$.[102].

Photoexcitation of indoleninedicarbocyanines initially in *cis*-form gives long-lived *trans*-isomers together with short-lived di-*cis*-isomers (k_{relax} respectively ~10^2 and ~10^6 s^{-1}).[132,269]. The latter are sterically hindered and are found in low quantum yields (0.01–0.1). Dyes having a shorter polymethine chain can also form sterically hindered di-*cis*-photoisomers[275].

The efficiency of photoisomerisation effected by rotation of large fragments of the molecule is substantially dependent on the viscosity of the medium: increase in viscosity diminishes the probability of formation of a photoisomer[131,272] and its rate of relaxation[276]. Photoisomerisation is influenced also by the temperature[276] and the solvent[271,279]. Thus a ketocyanine isomerises in a non-polar solvent ($\phi_{isom} = 0.5$) but

not in alcohol[279], owing to predominance of the non-polar structure of the photoisomer.

Merocyanine dyes, like carbocyanines, are capable of photoisomerisation[280–282]. From a singlet excited state both short- and long-lived photoisomers are formed (k_{relax} respectively ~100 and ~1 s^{-1}), whereas a triplet state yields only the latter[280,281]. They are formed by rotation about the $C_{(2')}$–$C_{(8')}$ and $C_{(5)}$–$C_{(9')}$ bonds respectively[281]. The photoisomerisation rate constant depends on the proton-donor power and the polarity of the solvent[282].

Table 7. Influence of substituents in polymethine chain of 3,3'-diethylthiacarbocyanine on quantum efficiences, rate constants, and activation energies of *cis–trans*-photoisomerisation[131–134,175,264,274].

Substituents	Isomer	φfl	$\varphi$is	φisom	k_1, s^{-1}	k_{relax}, s^{-1}	E_a, kcal $mole^{-1}$
None	*cis*	0.05	<0.001	0.95	$4.6 \cdot 10^2$	$1.6 \cdot 10^2$	15
9-Methoxy	*cis*	0.015	0.20	<0.001	$3.3 \cdot 10^3$	—	—
8-Fluoro	*trans*	0.03	<0.001	0.99	$1.6 \cdot 10^4$	$1.9 \cdot 10^2$	13.3
9-Fluoro	*cis*	0.55	0.03	0.4	$8.2 \cdot 10^2$	$3.2 \cdot 10^3$	11.3
8,9-Difluoro	*trans*	0.005	0.16	0.83	$9.3 \cdot 10^5$	$1.0 \cdot 10^5$	9.6
8,9,10-Trifluoro	*trans*	≤0.0005	—	0.6	$\gg 3 \cdot 10^5$	$5.0 \cdot 10^6$	7.3
8,10-Dimethyl	—	0.0024	0.005	0.9	—	$1.8 \cdot 10^4$	10.5

Thioindigo and its derivatives are capable of *cis–trans*-photoisomerisation[65,66,195,196,227,283–287]. With thioindigo and 6,6'-diethoxythioindigo the reaction involves a triplet state common to *cis*- and *trans*-forms. In the triplet state fragments of the molecule are turned through 90° relative to the ethylenic bond[196]. Involvement of the triplet state of thioindigo in isomerisation follows from results on sensitised population of the triplet level of the dye molecule[286] and on inhibition of the *trans* → *cis* transition by oxygen[227,287], as well as from comparison of rates of triplet deactivation and photoisomer accumulation[196]. However, recent work[307,308] on the mechanism of the photoisomerisation of *trans*-thioindigo using a picosecond laser casts doubt on involvement of a triplet state in isomerisation.

Azomethine dyes undergo *syn–anti*-isomerisation about the carbon–nitrogen double bond[288]. Two mechanisms are possible, one (torsion) consisting in rotation about this bond, and the other (inversion) in rotation of a fragment in the plane of the molecule through 120° about the nitrogen atom. Experimental results indicate that both mechanisms operate[289], isomerisation occurring in both singlet excited and triplet states[290,291]. In azo-dyes of the Picramine R group[292] *cis–trans*-photoisomerisation takes place from a singlet excited state[191].

2. Electron Transfer

Electron transfer is the most common photochemical reaction of dyes[234]. It can occur in both singlet excited and triplet states. Interaction of excited molecules with electron donors or acceptors will inevitably produce additional paths for degradation of the excitation energy. Thus a consequence of electron transfer is to shorten the lifetime of excited molecules in the presence of a quenching additive, in conformity with the Stern–Volmer equation. Thus the singlet lifetime τ_S^* of Thionine is shorter in the presence of iron(II) chloride or sulphate in aqueous solution at pH 2.[129]

Study of the quenching of singlet excited states usually involves measurement of the relative fall in efficiency or intensity of fluorescence. If the dye molecules do not form non-luminescent complexes with quenching additives, the fall in efficiency and the shortening of the lifetime τ_S^* are described by the same Stern–Volmer formula. A fall in fluorescence efficiency has been found for Thionine in the presence of iron(II), manganese(II), cerium(III), and caesium(I) in water at pH 2.5,[293] Rhodamine 101 in the presence of methanolic amines[294], and Methylene Blue in the presence of iron(II) in 0.01 M hydrochloric acid[149]. The rate constant for the quenching of singlet excited states of Thionine molecules by iron(II) cations is $k_q = 3.5 \times 10^9$ M^{-1} s^{-1},[129] identical with the 3.6×10^9 M^{-1} s^{-1} calculated from the Stern–Volmer dependence for the fall in fluorescence efficiency[293] and for the lifetime of these singlet states[129]. Thus quenching of fluorescence in the Thionine–iron(II) system is due solely to electron transfer. Formation of complexes in the ground state is possible between Thionine and the sulphate anion[293].

Table 8. Rate constants k_q for quenching of the triplet state of dyes by electron donors and acceptors.

Dye	Solvent	Donor	Acceptor	k_q, M^{-1} s^{-1}	Ref.
Eosin	water, pH 7.1	(-)-tryptophan	—	$8.4 \cdot 10^8$	[247]
»	water, pH 6.2	—	ferricyanide	$7.5 \cdot 10^8$	[246]
»	water, pH 7.2	edta	—	$5.0 \cdot 10^5$	[60]
»	water, pH 7.2	allylthiourea	—	$3.4 \cdot 10^5$	[60]
Rhodamine 6G	water, pH 6	—	*p*-benzoquinone	$2.5 \cdot 10^9$	[116, 124]
»	water, pH 6	ascorbic acid	—	$8.0 \cdot 10^8$	[116, 124]
»	water, pH 6	hydroquinone	—	$2.0 \cdot 10^9$	[116, 124]
»	water, pH 6	ferrocyanide	—	$8.0 \cdot 10^9$	[116, 124]
»	water, pH 6	—	ferricyanide	$5.0 \cdot 10^9$	[116, 124]
Thionine	water, pH 7.1	(-)-tryptophan	—	$3.9 \cdot 10^9$	[247]
»	water, pH 7.1	allylthiourea	—	$1.1 \cdot 10^7$	[247]
»	water, pH 2.5	—	Fe^{3+}	$9.0 \cdot 10^4$	[183]
»	water, pH 2.5	Fe^{2+}	—	$6.1 \cdot 10^7$	[183]
»	methanol, pH 8.6	hydroquinone	—	$2.5 \cdot 10^9$	[248]
»	methanol, pH 8.6	thiourea	—	$7.5 \cdot 10^6$	[248]
»	acetonitrile	*p*-phenylenediamine	—	$5.9 \cdot 10^9$	[185]
Methylene Blue	water, 0.01M H_2SO_4	Fe^{2+}	—	$5.5 \cdot 10^6$	[220]
»	water, 0.04M KH_2PO_4	—	ferricyanide	$1.4 \cdot 10^{10}$	[220]
»	methanol	triethylamine	—	$4.7 \cdot 10^7$	[295]
»	methanol	aniline	—	$1.1 \cdot 10^{10}$	[295]
»	acetonitrile	*p*-phenylene-diamine	—	$1.4 \cdot 10^{10}$	[189]
»	acetonitrile	perylene	—	$3.2 \cdot 10^9$	[189]
»	acetonitrile	9,10-dimethy-lanthracene	—	$3.7 \cdot 10^7$	[189]
Oxonine	water, pH 8	edta	—	$1.5 \cdot 10^7$	[296]
»	methanol	allylthiourea	—	$1.8 \cdot 10^6$	[182]
Biscyanine	propanol	—	nitroxyl	$(1—10) \cdot 10^7$	[225]
3,3'-Diethyl-9-methoxy-carbocyanine	propanol	ascorbic acid	—	$2.5 \cdot 10^8$	[181]
»	propanol	2-naphthylamine	—	$2.0 \cdot 10^6$	[181]
»	propanol	—	*p*-benzoquinone	$6.7 \cdot 10^8$	[181]
»	propanol	—	*m*-dinitro-benzene	$2.2 \cdot 10^9$	[181]
»	propanol	—	methylviologen	$1.4 \cdot 10^8$	[181]

Quenching of triplet states by electron donors and acceptors has been investigated in thiazine[171,182–189,215,218,220,247,248,295,296], xanthen[59,60,116,124,246,247,297], acridine[192–194], polymethine[131,181,225], and other dyes[234] (Table 8).

The Stern–Volmer type of linear dependence found experimentally between the relative shortening of the lifetime of singlet and triplet molecules and the concentration of the

quenching additive is a direct indication of the possibility of electron transfer. It must be borne in mind that this type of relationship is satisfied by other processes, e.g. energy or hydrogen transfer. Electron transfer involving excited dye molecules is characterised firstly by the formation of solvated radical-ions (or radicals) and secondly by a correlation between the quenching rate constant and the donor or acceptor properties of the quencher.

Flash and laser photolysis have been used to determine the absorption spectra of one-electron oxidation and reduction products of fluorescein[297], rhodamine[116,123,124,298], thiazine[182-185,187-189,295], acridine[182,228], polymethine[131,181,225], and other dyes.

In polar media electron transfer between a triplet dye molecule (acceptor) and a quencher molecule (donor) leads to formation of a solvent-separated radical-pair[234]:

$$A(T) + D \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A(T)\ldots D \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} A^{\dot{-}}\ldots D^{\dot{+}} \begin{cases} \xrightarrow{k_{30}} A + D \\ \xrightarrow{k_{34}} A^{\dot{-}} + D^{\dot{+}} \end{cases}$$

This either dissociates into solvated radical-ions or recombines with formation of the original reactants in the ground state; involvement of a triplet excited complex has also been suggested[184,248,301].

The quenching rate constant is given by the formula[301]

$$k_q = k_{12}\left[1 + \frac{k_{21}}{k_{30}}\exp\left(\frac{\Delta G_{23}^{\neq}}{RT}\right) + \frac{k_{21}}{k_{30}+k_{34}}\exp\left(\frac{\Delta G_{23}}{RT}\right)\right]^{-1}, \qquad (12)$$

The relation between the free energy of activation $\Delta G_{23}^{\neq}$ and the change in free energy of electron transfer ΔG_{23} is established by means of the correlation[299]

$$\Delta G_{23}^{\neq} = \frac{\Delta G_{23}}{2} + \left[\left(\frac{\Delta G_{23}}{2}\right)^2 + (\Delta G_{23}^{\neq}(0))^2\right]^{1/2} \qquad (13)$$

in which $\Delta G_{23}^{\neq}(0)$ is the free energy of activation when $\Delta G_{23} = 0$. It follows from (12) and (13) that k_q is independent of ΔG_{23} for exothermic reactions ($\Delta G_{23} < 0$), whereas $\ln k_q$ decreases linearly with increase in ΔG_{23} for endothermic reactions ($\Delta G_{23} > 0$). Good agreement has been found between the experimental and the calculated dependence of k_q on ΔG_{23} over wide ranges of the latter for Thionine[185,300], Methylene Blue[189,220], eosin[255], Acridine Orange[194,301] and its 10-methyl derivative[194], and *o*-methylfluorescein methyl ester[185], which confirms the electron-transfer mechanism of quenching of the triplet state.

Electron transfer can occur in both singlet excited and triplet states. With dilute solutions and low concentrations of quenching additives it takes place solely in the triplet state. Evidence of involvement of this state of dye molecules in electron transfer is provided by quenching results and by kinetic analysis of its deactivation and the accumulation of radical-ions (or radicals), which are products of electron transfer[234]. The role of the triplet state has been demonstrated in one-electron oxidation and reduction reactions of Thionine[171,182-184,215,248], Methylene Blue[185-189,218,295], fluorescein[59,204,297], eosin[204,246], erythrosin[59], Safranine T,[172] phenosafranine[172], Oxonine[296], Acridine Orange[192-194], Rhodamine 6G,[116,123,124] polymethine dyes[131,181], etc.

Electron transfer can occur not only as a result of diffusional encounters of a triplet dye molecule with an unexcited partner molecule (exogenous electron donor or acceptor) but also in the absence of foreign donor or acceptor molecules. In the latter case the partner may be another triplet molecule [triplet–triplet interactions (8)] or an unexcited molecule of the same dye [triplet–singlet interaction (11)]. Electron transfer by reactions (8) and (11) has been established for fluorescein[204], eosin[204], Rhodamine 6G,[116,123,124], and thiazine[187,204] and polymethine[131,222] dyes.

3. Other Reactions

Proton phototransfer involving dye molecules has been considerably less studied. The acid–base properties in both ground and electronically excited states are characterised by the protolytic equilibrium exponent pK. Values of $pK_{S_0,T}$ in ground and triplet states are usually determined from the pH dependence of the $S_0 \to S_n$ and $T_1 \to T_n$ absorption spectra, and those of pK_{S*} in the singlet excited state from that of the fluorescence spectra. Determinations of pK_{S_0}, pK_{S*}, and pK_T have been made on xanthen, thiazine, azine, and other dyes[59]. It follows from Table 9 that excitation of thiazine dye molecules to a triplet state appreciably facilitates proton addition to the cation with formation of the protonated form. Data on acid–base equilibrium constants for thiazine dyes and the relative proton affinities estimated therefrom for molecules in ground and triplet states are confirmed by calculations of the distribution of electron density for Thionine in ground, singlet excited, and triplet states[302]. These show that the basic properties of Thionine are significantly stronger in the triplet than in the unexcited state, with the singlet excited state occupying an intermediate position. A similar situation is found for other thiazine dyes.

Table 9. Acid–base equilibrium constants of dye molecules in ground, singlet excited, and triplet states[59].

Dye	pK_{S_0}	pK_{S*}	pK_T
Fluorescein (monoanion)	6.7	—	7.0
Eosin (monoanion)	4.3	—	<4
Erythrosin (monoanion)	5	—	5
Thionine	−0.33	3.1	6.3
Methylene Blue	<1	—	6.7
Methylene Green	<1	—	7.5
New Methylene Blue	<1	—	7.5
Azure	<1	—	7.7
Safranine T	0.1	—	6
Phenosafranine	0	—	6

A substantial difference between pK_T and pK_{S_0} is observed also with azine dyes (Safranine T, phenosafranine). Their example also reveals a higher basicity of molecules in the triplet state than in the singlet states S_0 and S_1. However, the above rule does not hold for xanthen dye molecules: pK_T and pK_{S_0} have closely similar values (Table 9).

Laser excitation has been used[303] for the direct determination of kinetic parameters of proton transfer involving triplet Thionine. The rate constant is found to be close to the diffusion constant[303,304].

Among little investigated but important photoreactions of dyes is photodissociation. It has been shown for leuco-cyanides of triarylmethane dyes (Malachite Green, Brilliant Green) that a coloured form—the dye cation—appears on ultraviolet exposure of solutions in polar media[305,306]. From direct measurements of the rate of formation of the cation of Malachite Green[305] and data on the sensitised population of the triplet level of the leuco-cyanide of Brilliant Green[306] it is concluded that a singlet excited state is involved in photodissociation.

Photodissociation of the *p*-azido-derivative of Malachite Green has been studied in an alcohol–ether matrix at 77 and 300 K.[309] At the latter temperature the quantum efficiency

of the photoelimination of nitrogen increases from 0.001 to 0.1 with change in the exciting wavelength from 600 to below 350 nm. A predissociation mechanism of rupture of the nitrogen–nitrogen bond is regarded as the most probable.

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Thus laser techniques have permitted the investigation in dye molecules of many primary photoprocesses lasting as little as 10^{-12} s. The laws of photophysical and primary photochemical reactions established for dyes of various classes are common to many organic compounds and biologically active substances. Research on primary photoprocesses in dye molecules constitutes an important branch of photochemistry–molecular photonics.

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Bimetallic Transition Metal Hydride Complexes

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The literature data on bimetallic transition metal hydride complexes containing metal-hydrogen bonds and non-transition metal atoms are described systematically and discussed. The principal methods of synthesis of these compounds and ways of stabilising them in the lowest oxidation state by cyclopentadienyl and other electron-donating ligands are considered. The characteristics of the changes in the transition metal-non-transition metal and metal-hydrogen bond types as a function of the electronic configuration and the ligand environment of the metal atoms forming part of the bimetallic hydride complex are noted. The influence of complex formation on the geometrical parameters and spectrochemical characteristics of the metal-hydrogen bond are discussed.
The bibliography includes 191 references.

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I. INTRODUCTION

The successful preparation of catalytic systems of the Ziegler–Natta (Z–N) type for the hydrogenation and isomerisation reactions of olefins at the beginning of the 1960s led to a rapid increase in the number of publications, mainly patents, devoted to studies and applications of a wide variety of catalysts and cocatalysts for these reactions. At the present time there is no doubt that the active centres of the catalysts contain metal–hydrogen bonds[1–3]. The individual hydrides of Group VIII metals catalysing the hydrogenation of olefins have been studied in fair detail, particularly the rhodium, iridium, and ruthenium compounds. Their structures and the mechanisms of their hydrogenation have been considered in a number of reviews[4–6].

At the same time the reaction mechanism and the structure of the active centres of the classic Z–N system have not so far been finally elucidated.

This is because of the high sensitivity of the systems to oxidation and the consequent considerable scatter and poor reproducibility of the experimental data. Furthermore, several catalytic reactive complexes containing the transition metal (TM) in the lowest oxidation states[3] are as a rule formed in the course of the reaction[7,8].

It has been suggested that the low-valence state is stabilised as a result of the formation of a complex with the cocatalyst—a non-transition metal compound[3,9]. Since usually alkyl or hydride derivatives of aluminium and more rarely lithium alkyls and Grignard reagents are used as the cocatalyst, the active centres in such cases may be bimetallic hydride complexes (BHC) containing both a transition and a non-transition metal.

Complexes of this type have been studied in solutions. A comparatively small number of BHC have been isolated in a pure state and investigated. However, on the basis of the available data one cannot reach any definite conclusion concerning the relation between the structure of the BHC and their catalytic activity because the individual compounds have not as a rule been used in catalytic processes.

In monographs[10] and review articles[4,5] devoted to transition metal hydrides and also the application of the Z–N catalysts in the hydrogenation reactions of unsaturated compounds[2,3] little attention has been devoted to the BHC. Admittedly, recently a detailed review has been published on transition metal hydroborates belonging to the class of BHC.[11] In the present study these comparatively thoroughly investigated compounds will therefore be considered only in relation to the hydroaluminates. It is noteworthy that the M–H–B bridge bond in the transition metal hydroborate is not apparently involved in the catalytic steps and the activity of the compounds $M(BH_4)_nL_m$ or the MX_n–$M'(BH_4)_m$ systems is probably related to the products of their reactions or decomposition with formation of the M–H bond[12].

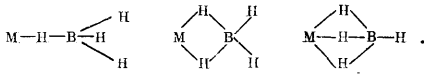
II. CLASSIFICATION OF BIMETALLIC HYDRIDE COMPLEXES

As regards the nature of the metal–hydrogen bond, BHC can be divided into four main types. In the first three the transition metal is linked to the non-transition metal via a hydrogen atom, while in the fourth there is a direct linkage.

The first type includes ionic or similar "inorganic" transition metal tetrahydroaluminates having the general formula $M(AlH_4)_m$, for example, $Y(AlH_4)_3$ [13] and $Nb_2(AlH_4)_5$.[14] The

tetrahydroaluminate group in these compounds consists of a more or less distorted isolated $[AlH_4]^-$ tetrahedron. This type includes also the ionic complexes of Group VIII metals such as $L_nFe^+[AlH_2X_2]^-$.[15]

An increase in the strength of the M–H bond leads to the formation of covalent three-centre bridge bonds. The most striking representative of the second type of BHC are the thoroughly investigated transition metal tetrahydroborates. All the possible varieties of bridges with one[16], two, and three[11] hydrogen atoms are known for these compounds:



Among the aluminium-containing BHC, compounds are known with both single bridges, such as $[Cp(C_5H_4).TiHAlEt_2]_2$ [17] and $Cp_2Ta(H)_2HAlMe_3$,[18] and double bridges, such as $Cp_2TiH_2AlEt_2$ [19] and $Cp_2NbH_2AlH_2$.[20]

A further increase in the strength of the M–H bond together with a weakening of the H–E bond lead to the formation of ionic compounds of the third type containing a transition metal linked to hydrogen atoms in the anion ($Cp_2TiH_2^-MgHal^+$) [21] or the cation $\{[L_mNiH]^+[AlCl_4]^-\}$.[22]

The fourth type includes complexes containing direct (covalent or donor–acceptor) metal–metal bonds, such as, for example, the "inorganic Grignard reagents" $Cp_2Mo(H).MgBr.2THF$ (THF = tetrahydrofuran) [23] or the adducts of Cp_2MoH_2 with halogenoalanes[24].

Naturally the proposed classification of BHC is fairly arbitrary. The real compounds may contain features of two types [for example, the compounds $M(AlH_4)_n$ have the features of both the first and second types] or may contain different types of bonds [for example, there are both terminal and bridging hydrogen atoms in $Cp_2Zr(H)BH_4$].[25]

III. METHODS OF SYNTHESIS OF BIMETALLIC HYDRIDE COMPLEXES

The sources of hydride hydrogen in the formation of the M–H bond in BHC may be individual hydrides of transition and non-transition metals, molecular hydrogen, alkyl groups, etc. The M–H bonds are then formed directly during the synthesis of the BHC or as a result of the substitution of alkyl groups, halogens, etc. in the bimetallic non-hydride complexes by the hydrido-ligand.

1. Reactions Involving Individual Transition Metal Hydrides

Stable binary transition metal hydrides MH_x, where x is usually 0.5–2, with a "metallic" metal–hydrogen bond are inactive in the synthesis of BHC. A directed two- or three-centre M–H bond is formed only in compounds containing stabilising electron-donating ligands (phosphines, carbon monoxide, cyclopentadienyl groups, etc.). However, since phosphine and carbonyl complexes are as a rule coordination-saturated, they are involved only extremely rarely in complex formation reactions with transition metal compounds (see Section VII below).

The cyclopentadienyl compounds Cp_2MH_n, whose interaction with Lewis acids leads to the formation of BHC of various types, constitute an exception.

The reaction of $(Cp_2ZrH_2)_x$ with $AlMe_3$ in benzene gives rise to a compound having the composition $(Cp_2ZrH_2.AlMe_3)_2$,[26] which may contain terminal Al–H bonds in the anion $[AlHMe_3]^-$:

$$(Cp_2ZrH_2)_x + xAlMe_3 \xrightarrow{20°,C_6H_6} \frac{x}{2}[Cp_2ZrH(HAlMe_3)]_2 \quad (1)$$

BHC containing the M–H–Al bridge bond have been obtained by an analogous reaction with participation of Cp_2TaH_3:[8]

$$Cp_2TaH_3 + AlEt_3 \xrightarrow{20°,C_6H_6} Cp_2Ta(H_2)HAlEt_3 \quad (2)$$

Direct M–E bonds are formed on interaction of Lewis acids with compounds of Group VI and VII metals having an unshared pair: Eqn.(3),[27] Eqn.(4),[24–28] and Eqn.(5).[29,30] The reduction of the metal to a lower oxidation state does not then take place:

$$Cp_2WH_2 + AlEt_3 \xrightarrow{20°,C_6H_6} Cp_2W(H)_2AlEt_3 \quad (3)$$

$$Cp_2ReH + BF_3 \xrightarrow{33°,\text{several days}} Cp_2Re(H)BF_3 \quad (4)$$

$$Cp_2MoH_2 + ZnCl_2 \rightarrow Cp_2MoH_2ZnCl_2 \quad (5)$$

Sometimes reactions of this kind are accompanied by the elimination of a hydrocarbon:

$$Cp_2MoH_2 + \text{iso-PrMgBr} \xrightarrow[-C_6H_6]{Et_2O} [Cp_2Mo(H)Mg(\text{iso-Pr})(\mu\text{-}Br)_2Mg(OEt_2)]_2 \xrightarrow{THF} 2Cp_2Mo(H)MgBr\cdot 2THF + 2\ \text{iso-PrMgBr} \quad (6)$$

A non-transition metal hydride may be involved in such reactions: Eqn.(7),[31] Eqn(8),[32] and Eqn.(9):[24]

$$(Cp_2TiH)_2 + B_2H_6 \xrightarrow{0°,THF} Cp_2TiBH_4 \quad (7)$$

$$(Cp_2ZrH_2)_x + x\,HAl(\text{iso-Bu})_2 \xrightarrow{20°,C_6H_6} Cp_2Zr(H)_2HAl(\text{iso-Bu})_2 \quad (8)$$

$$Cp_2MoH_2 + AlH_{3-n}Cl_n \xrightarrow{C_6H_6} Cp_2Mo(H)_2AlH_{3-n}Cl_n \quad (9)$$

2. Reactions with Participation of Non-Transition Metal Hydrides

This constitutes the most effective and promising methods of synthesis of BHC. Non-transition metal (mainly aluminium) hydrides undergo exchange reactions and addition reactions with transition metal salts or complexes to form BHC. With a rare exception[33], these reactions are carried out in ethyl ether or THF. Transition metals in the highest oxidation states are then usually reduced, for example, Fe^{III} is reduced to Fe^{II} [Eqn.(10)],[34] Ta(V) is reduced to Ta(IV) [Eqn.(11)],[35] and Ti(IV) is reduced to Ti(III) [Eqn.(12)]:[36,37]

$$FeCl_3 + LiAlH_4 \xrightarrow{-80°,Et_2O} Fe(AlH_4)_2\downarrow + H_2 + AlH_3 + LiCl\downarrow \quad (10)$$

$$TaBr_5 + LiAlH_4 \xrightarrow{-80°,Et_2O} [TaH_n(AlH_4)_{4-n}\cdot n\,AlH_3]\downarrow + H_2 + AlH_3 + LiBr \quad (11)$$

$$Cp_2TiCl_2 + LiAlH_4 \xrightarrow{20°,Et_2O} Cp_2TiAlH_4 + AlH_3 + LiCl \quad (12)$$

When the salts of transition metals in the lowest oxidation states are employed, the usual exchange reactions [reactions (13) [38] and (14) [39,40]] take place:

$$Li_2MnBr_4 + LiAlH_4 \xrightarrow{-80°,Et_2O} Mn(AlH_4)_2 + LiBr \quad (13)$$

$$(Cp_2TiCl)_2 + NaAlH_4 \xrightarrow{20°,THF} Cp_2TiH_2AlH_2 + NaCl \quad (14)$$

The 1,1′-methylenebiscyclopentadienyltitanium hydroaluminate $CH_2(C_5H_4)_2TiH_2AlH_2$, which is almost insoluble in ethyl ether and THF, has been obtained in a pure state only via the exchange reaction[41]

$$CH_2(C_5H_4)_2TiBH_4 + LiAlH_4 \rightarrow CH_2(C_5H_4)_2TiAlH_4\downarrow + LiBH_4 \quad (15)$$

Other hydroaluminates, insoluble or only slightly soluble in organic solvents, for example, $Zr(AlH_4)_4$, can also be obtained by this method.

The interaction of $Al(iso\text{-}Bu)_3$ and $AlH(iso\text{-}Bu)_2$ with Cp_2TiCl_2 or Cp_2VCl_2 leads to the formation of $Cp_2TiHClAl(iso\text{-}Bu)_2$ and $Cp_2TiH_2Al(iso\text{-}Bu)_2$ even for the ratios Al/Ti = 2 : 1 and 3 : 1:[42–47]

$$Cp_2Ti(V)Cl_2 + HAl(iso\text{-}Bu)_2 \rightarrow Cp_2Ti(V)H_2Al(iso\text{-}Bu)_2 + H_2 + ClAl(iso\text{-}Bu)_2. \quad (16)$$

It has been suggested that these compounds are formed either owing to the presence of admixtures of hydrides in AlR_3 or as a result of the disproportionation reaction

$$Al(C_2H_5)_3 \rightleftarrows AlH(C_2H_5)_2 + C_2H_4 \quad . \quad (17)$$

$Cp_2TiH_2AlMe_2$ has been obtained in a different way, via the reaction of $(Cp_2TiCl)_2$ with $NaAlH_2Me_2$ in ArH.[48,49]

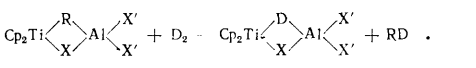
Reactions involving the addition of the aluminium hydride derivatives $AlH_nX_{3-n}.mL$, where $n = 1–3$, $m = 0$ or 1, and X = Hal, to biscyclopentadienyltitanium chloride, which are carried out in inert and, more rarely, solvating solvents, have been described[36,45,50,51]:

$$Cp_2TiX + AlH_nX_{3-n}\cdot L \xrightarrow{Et_2O,\ ArH} Cp_2TiH_nAlX_{4-n}\cdot L \quad . \quad (18)$$

These BHC are formed as intermediates in the interaction of Cp_2TiCl_2 with $LiAlH_4$.[37]

3. Activation of Molecular Hydrogen

It has been noted in a number of studies that the formation reactions of BHC in catalytic systems based on Cp_2TiCl_2 and alkali metal[52] and aluminium[44] alkyls are appreciably accelerated in a hydrogen atmosphere. The role of molecular hydrogen as a source of hydride hydrogen has been confirmed by experiments with deuterium[44] and in the hydrogenation of olefins in the presence of the $(Cp_2TiCl)_2$–$LiAlH_4$ system[53]:



$$+ RD \quad . \quad (19)$$

Reaction (19) can be regarded as the model reaction of the regeneration of the active centre in the catalytic hydrogenation of olefins.

4. The Cleavage of the Metal–Alkyl Bond

The cleavage of the M–Alk bond with formation of the M–H bond and an olefin [reaction (20)] has, with rare exceptions [for example, reactions (21) and (22)], no preparative value in the synthesis of BHC:[54,55]

$$M\text{–}Alk \rightleftarrows M\text{–}H + \text{olefin}; \quad (20)$$

$$(C_{10}H_8)(CpTiH)_2 + Al(C_2H_5)_3 \xrightarrow{C_6H_6} (C_{10}H_8)[CpTi(H)H_2Al(C_2H_5)_2TiCp] + C_2H_4; \quad (21)$$

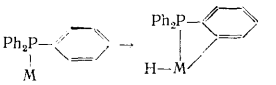
$$Cp_2TiCl_2 + C_2H_5MgCl \rightarrow Cp_2TiH_2^-MgCl^+ + MgCl_2 + C_2H_4 + C_2H_6 \quad . \quad (22)$$

However, reaction (20) plays an important role in catalytic isomerisation, polymerisation, and possibly metathetical reactions of olefins[56,57]. The alkyl groups are the source of hydride hydrogen in these substances[56]. It has been suggested that the $Cp_2TiH_2^-$ anion is formed via a stage involving the formation of the unstable anion $Cp_2TiR_2^-$.[58] Indeed a complex having the composition $[Na(THF)_x]^+[Cp_2TiR_2]^-$ has been obtained recently by the reduction of Cp_2TiR_2 with sodium naphthalide in THF.[59]

5. Transfer of Hydrogen from the Ligands to the Metal Atom

When Cp_2TiCl_2 is reduced with metallic magnesium in the presence of MgI_2 and also by lithium and sodium naphthalides in ether or THF, BHC with a double hydrogen bridge are formed[60–62]. The source of hydride hydrogen is in this instance the C_5H_5 group[61]. The formation of Cp_2TiH_2MgCl has also been noted in the reduction of Cp_2TiCl_2 with metallic magnesium in ethyl ether[58]. The reaction with metallic sodium in THF in the presence of $AlCl_3$ leads to the formation of $Cp_2TiH_2AlCl_2$ in 60% yield[63]. The same compound is formed on reduction of Cp_2TiCl_2 with metallic aluminium in THF.[64]

The reaction involving hydrogen transfer from the ligand is known to lead to the formation of "metallocene" hydrides {the "stable titanocene" $(C_{10}H_8)(CpTiH)_2$ and the "niobocene" $[Cp(C_5H_4)NbH]_2$} and also BHC such as $[Co(C_5H_4)TlHAlEt_2]_2$[17] and $(C_{10}H_8)[(C_5H_4)TiHAlEt_2]_2$.[54] These reactions proceed as a rule at elevated temperatures and lead to the formation of compounds with σ-π-linked cyclopentadienyl rings. The reaction mechanism is in all cases obscure. An analogous reaction has been described for arylphosphine complexes of transition metals[65]:



(23)

6. Reactions with Participation of the Solvent

In the extensive reduction of transition metals the source of hydrogen used for the formation of the M–H bond may also be the solvent, for example, ethyl ether in the reduction of Cp_2TiCl_2 with metallic magnesium [reaction (24)] and in the interaction of LiC_2H_5 with "metastable titanocene" [reaction (25)]:[58]

$$2Cp_2TiCl_2 + 5Mg + 4(C_2H_5)_2O \rightarrow 2Cp_2TiH_2^-MgCl^+ + MgCl_2 + 2Mg(OC_2H_5)_2 + 4C_2H_4; \quad (24)$$

$$(Cp_2Ti)_2 + 4C_2H_5Li + 2(C_2H_5)_2O \rightarrow 2Cp_2TiH_2^-Li^+ + 2LiOC_2H_5 + 5C_2H_4 + C_2H_6. \quad (25)$$

Nor can one rule out the possibility that the solvent "supplies" the hydride hydrogen in the synthesis of $Cp_2TiH_2AlCl_2$ from Cp_2TiCl_2 and Na in the presence of $AlCl_3$ in THF.[63]

IV. TRANSITION METAL TETRAHYDROALUMINATES

Transition metal tetrahydroaluminates without stabilising organic ligands, having the general formula $M(AlH_4)_n$, are known for Cu, Ag, Ce, V, Ti, Zr, Nb, Ta, Mn, Fe, and possibly Co.

The general method of synthesis of these compounds involves the exchange reactions of the salts with $LiAlH_4$ in ethyl ether at low temperatures (between −110° and −80 °C). Since the $M(AlH_4)_n$ are insoluble in ethyl ether, like LiCl, the products investigated in the early studies were mixtures of two substances[66,67]. Pure transition metal tetrahydroaluminates were obtained using MBr_n or the bromide complexes Li_mMBr_{n+m}:

$$Li_mMBr_{n+m} + n\,LiAlH_4 \xrightarrow{\sim 110°,\ Et_2O} M(AlH_4)_n + (n+m)\,LiBr \quad . \quad (26)$$

In certain cases the starting materials were perchlorates[68,69] and tetrahydroborates[70]. Transition metal tetrahydroaluminates are substances insoluble in organic solvents, whose colour varies from yellow to red-brown with increase of the number of *d* electrons. The $M(AlH_4)_n$ are as a rule readily

oxidised and on contact with air ignite spontaneously [$Y(AlH_4)_3$ [13] and tantalum[35] and niobium[14] compounds]. They are vigorously hydrolysed by water with evolution of the entire hydride hydrogen. An exception is the tantalum tetrahydroaluminate $TaH_2(AlH_4)_2$, in which the metal–hydrogen bonds are retained after hydrolysis according to infrared spectroscopy data [ν(M–H) = 1650 cm^{-1}]. The residual hydrogen (three atoms per tantalum atom) is evolved on treatment with alkali[35].

When $NbCl_5$ is made to react with an excess of $LiAlH_4$, tetrahydroaluminates in different oxidation states are formed depending on the temperature. The yellow complex $LiNb_2 \cdot (AlH_4)_7$ was obtained in the range between −120° and −70 °C, being converted into the dark-red $LiNb_2(AlH_4)_5$ on raising the temperature[67]. The reaction at room temperature leads to the formation of the brown niobium(II) complex $LiNb \cdot (AlH_4)_3$.[67,71] Analogous binary compounds are formed also with LiCl.[72] A complex formation reaction with LiBr has likewise been noted for yttrium and ytterbium tetrahydroaluminates[72].

Zirconium tetrahydroaluminate apparently forms anionic complexes too, since a white deposit of this compound dissolves in an excess of zirconium(IV) tetrahydroborate[70]. However, it is noteworthy that the complex-forming atom in this instance can also be the aluminium atom which is known to form complex anions, for example, $[Al(BH_4)_4]^-$.[73]

The decomposition of the majority of the tetrahydroaluminates $M(AlH_4)_n$ begins already at −50° and below. This accounts for the virtually complete lack of data concerning the synthesis of the tetrahydroaluminates of metals such as V, Cr, Au, and Ag as well as data on the chemical and physicochemical properties of other compounds. The relatively stable tantalum and yttrium tetrahydroaluminates are an exception. The thermal stability increases consistently on passing from the First to the Third Series of transition elements (within a single Group), for example, Ti < Zr and Nb < Ta, although there is no explicit regularity on passing from Group to Group. One can only note that the stability of the tetrahydroaluminates varies in parallel with the thermal stability of the corresponding tetrahydroborates and that its maximum corresponds to Groups I–V.

The use of differential thermal analysis (DTA) in combination with gas-volumetric measurements made it possible to determine the mechanisms of the thermolysis of certain tetrahydroaluminates. The instances described in the literature can be combined in four groups.

1. The reduction of the metal to the lowest oxidation states with retention of the metal–tetrahydroaluminate group bond:

$$M^{n}(AlH_4)_n \rightarrow M^{n-m}(AlH_4)_{n-m} + m\,AlH_3 + \frac{m}{2}\,H_2 \quad (27)$$

Examples are provided by the reduction of Nb(V) to Nb(III) [14] or Nb(II).[71] It has also been suggested that the synthesis of iron(II) and tantalum(IV) tetrahydroaluminates proceeds via a stage involving the formation of the unstable $Fe(AlH_4)_3$ [34] and $Ta(AlH_4)_5$.[35,66,67]

2. The decomposition to the free metal and aluminium hydride is most frequently encountered:

$$M(AlH_4)_n \rightarrow M + n\,AlH_3 + \frac{n}{2}\,H_2 \quad (28)$$

Certain niobium tetrahydroaluminates[67,71], $AgAlH_4$,[68] $Fe(AlH_4)_2$,[74] and possibly $Zr(AlH_4)_4$ [70] decompose in this way.

3. The decomposition to the free transition metal and aluminium has been observed for $Ce(AlH_4)_3$,[75] $Mn(AlH_4)_2$, $Co(AlH_4)_2$,[38] and $AgAlH_4$.[69] However, it is known that thoroughly dispersed transition metal powders catalyse the decomposition of aluminium hydride:

$$M(AlH_4)_n \rightarrow M + n\,Al + 2n\,H_2 \quad (29)$$

It is therefore extremely likely that reaction (29) proceeds via a stage involving the formation of AlH_3, which is unstable under the given conditions, and is a special case of reaction (28).

4. The decomposition to the transition metal hydride and aluminium hydride, which takes place without a change in the valence state of the transition metal, has been observed for tantalum [Eqn.(30)] [35] and copper[38] tetrahydroaluminates:

$$Ta(AlH_4)_n \rightarrow TaH_2(AlH_4)_2 + 2AlH_3 \quad (30)$$

The individuality of $CuAlH_4$ has been confirmed by the synthesis from it of an Na_3AlH_6 analogue—copper(I) hexahydroaluminate Cu_3AlH_6—by the low-temperature (−40 °C) treatment of the tetrahydroaluminate with THF.[76]

There are no literature data concerning the direct or indirect determination of the structures of transition metal tetrahydroaluminates. The only physicochemical method used in the study of these compounds is infrared spectroscopy, but the data thus obtained are very scanty. This is evidently associated with the considerable difficulties in the low-temperature measurement of the spectrum. The infrared spectra of the transition metal tetrahydroaluminates contain absorption bands in the range 1500–1850 cm^{-1} which can be assigned to the stretching vibrations of the terminal Al–H bonds. The wave numbers ν for these vibrations in $Nb_2(AlH_4)_5$ (1500 cm^{-1}) [72] (1850 cm^{-1}),[67] $Ti(AlH_4)_4$ (1615 cm^{-1}),[77] $TaH_2(AlH_4)_2$ (1600 cm^{-1}), $Fe(AlH_4)_2$ (1690 cm^{-1}), $Y(AlH_4)_3$ (1840 cm^{-1}), and $Yb(AlH_4)_2$ (1800 cm^{-1}) [72] are close to the values of ν(Al–H) for ionic lithium (1780 cm^{-1}), sodium (1680 cm^{-1}), tetramethylammonium (1660 cm^{-1}),[78] and magnesium (1850 cm^{-1}) [79] tetrahydroaluminates.

Bearing in mind the physical and spectroscopic characteristics of the transition metal tetrahydroaluminates $M(AlH_4)_n$, one can assume that, in contrast to the corresponding tetrahydroborates, these are compounds with predominantly ionic M–AlH_4 bonds and slightly distorted tetrahedral anions $[AlH_4]^-$, i.e. apparently have structures similar to those of alkali and alkaline earth metal tetrahydroaluminates.

V. BISCYCLOPENTADIENYL BIMETALLIC HYDRIDE COMPLEXES

The biscyclopentadienyl complexes of transition metals, which can be regarded as products of the addition of transition metal biscyclopentadienyl hydrides[80,81] to Lewis acids or bases are most interesting from the theoretical and practical points of view.

Two types of transition metal biscyclopentadienyl hydride derivatives have been described in the literature: the biscyclopentadienyl hydrides proper with the general formula $(\eta^5\text{-}C_6H_5)_2MH_n$ and the so-called "metallocene hydrides" in which the metal–hydrogen bond is formed as a result of a rearrangement in an unstable "metallocene" Cp_2M with transfer of a hydrogen atom from the Cp ring to the metal atom.

According to quantum-chemical calculations on Cp_2ML_n molecules, where n = 1–3,[82–85] the metal atom in the Cp_2M fragment with inclined rings has three hybrid orbitals, used in the formation of bonds with ligands and located in a plane with yz symmetry.

The 18 electron rule holds for the majority of the compounds investigated[85].

1. Group IVA

BHC of the first three types are known for the elements of the titanium subgroup. The greatest number of compounds have been described for titanium owing to the vigorous

studies of the Cp_2TiCl_2–reductant systems with catalytic activity in the fixation of molecular nitrogen and the polymerisation and hydrogenation of olefins. However, one should note that in the vast majority of cases individual compounds were not isolated and they were identified solely by indirect methods, mainly by EPR. Only recently have studies been published in which these substances and systems have been investigated by other physicochemical methods.

Thus it has been shown[39,40] that the interaction of $(Cp_2TiCl)_2$ with $NaAlH_4$ in THF leads to the formation of Cp_2TiAlH_4 [Eqn.(14)]. Indeed, according to calorimetric titration (CT) data, this reaction proceeds in a single stage, whose heat is 140 kJ mol^{-1}, terminates following the attainment of the ratio Al : Ti = 1 : 1,[86] and differs from the analogous reaction involving $LiBH_4$ [reaction (31)], which leads to the formation of a complex with the ratio B : Ti = 2 : 1:[87]

$$Cp_2TiCl + LiBH_4 \xrightarrow{Et_2O} LiCl + Cp_2TiBH_4 \underset{-LiBH_4}{\overset{LiBH_4}{\rightleftarrows}} Li[Cp_2Ti(BH_4)_2] \quad . \quad (31)$$

However, in a study of the catalytic properties of the $(Cp_2TiHal)_2$–$LiAlH_4$ system[53] it was established that the reaction results also in the formation of a catalytically active unstable BHC having the composition $(Cp_2Ti)_2AlH_4Cl$, which is not manifested on the CT curves.

The reaction of $(Cp_2TiCl)_2$ with the chloroalanes AlH_nCl_{3-n} [Eqn.(18)], proceeds according to CT data, with a heat change of 171 kJ mol^{-1} for n = 3 and 92 kJ mol^{-1} for n = 2.[36] In the latter case the reaction proceeds in two stages and terminates for the ratio Al : Ti = 2 : 1 with formation of the unstable complex $Cp_2TiH_2AlCl_2.AlH_2Cl$.[51] The study of the interaction in the $(Cp_2TiCl)_2$–AlH_2Cl system by dielectrometric titration[36,51] showed that $Cp_2TiH_2AlCl(H)$ is formed also via an intermediate stage involving the formation of an unusual conducting compound with the ratio Al : Ti = 1 : 3.

Analogous complexes, also detected by the CT method, exist likewise in the $(Cp_2TiCl)_2$–$AlH_nCl_{3-n}.L$ systems with n = 0 and 1.[88] The heats of reaction (32) are 58.5 kJ mol^{-1} for n = 0 and 44.9 kJ mol^{-1} for n = 1:

$$3Cp_2TiCl + AlH_nCl_{3-n}\cdot L \xrightarrow{C_6H_6} (Cp_2Ti)_3AlH_nCl_{6-n}, \; n = 0, 1 \quad . \quad (32)$$

Since the dipole moments of these complexes are close to zero[88], the latter apparently have symmetrical structures with a hexacoordinate aluminium atom in the centre of an octahedron, i.e. they resemble the structures of the known complexes of Cp_2TiCl with zinc, beryllium[89,90], and manganese[91] chlorides having the composition $(Cp_2Ti)_2M'Cl_4$. The proposed model has been confirmed by EPR [64,88] and infrared spectroscopic[50] data. Although further interaction of $(Cp_2Ti)_3AlH_n.Cl_{6-n}$ (n = 0 and 1) with $AlH_nCl_{3-n}.L$ does take place, it does not entail a heat change[88]. The EPR signal characteristic of the BHC $Cp_2TiH_2AlCl_2$ gradually appears in reaction (32) with an excess of dichloroalane in solution[51,88], i.e. a reaction analogous to reaction (33) takes place[42,43]:

$$Cp_2TiCl_2AlR_2 \underset{-ClAlR_2}{\overset{+HAlR_2}{\rightleftarrows}} Cp_2TiCl(H)AlR \underset{-ClAlR_2}{\overset{+HAlR_2}{\rightleftarrows}} Cp_2TiH_2AlR_2 \quad . \quad (33)$$

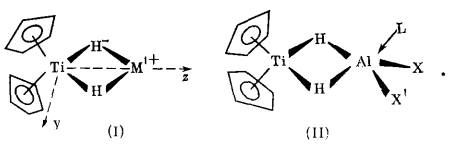
Solutions of the BHC Cp_2TiH_2M', where M' = Li, Na, MgHal, or AlX_2 have the intense violet colour characteristic also of other titanium(III) compounds containing two hydrogen bridges in the molecule—$(Cp_2TiH)_2$ [31] and $Cp_2TiH_2BH_2$.[92] In contrast to the halide and alkyl bridges, the hydride bridges are not decomposed by Lewis bases, which indicates their high strength. This is also confirmed by the displacement of the equilibrium in reaction (33) to the right even in the presence of a 50–100-fold excess of AlR_3 [42] and by direct thermochemical measurements.[37,51,86,88] The most informative method for the study of the paramagnetic BHC of titanium(III), vanadium(IV), iron(I), etc. in solution is EPR. The EPR spectra of BHC with the mixed bridges  are doublets as a consequence of the splitting by a single ^1H nucleus (J = 1/2) with a hyperfine coupling constant (HFC) a_H = 3.5–9.1 G (Table 1). The hyperfine structure (HFS) of the spectra of BHC with a double hydrogen bridge is due to the interaction of the unpaired electron with two equivalent hydrogen nuclei, which gives rise to the splitting of the spectral lines into a triplet in which the intensity ratios are 1 : 2 : 1 (observed, for example, in the spectra of magnesium-containing BHC [21,49,52,60,61]), and with the magnetic nucleus of the non-transition metal. The fundamental motif in the EPR spectrum is then a quartet for the lithium- and sodium-containing compounds ($J_{^7Li} = J_{^{23}Na}$ = 3/2) [40,52,58,60,95] and a sextet for the hydroaluminate complexes Cp_2TiH_2AlXX' ($J_{^{27}Al}$ = 5/2). The form of the spectrum is determined by the ratio of the HFC constants a_H and a'_M. In certain cases it is impossible to resolve the HFS of the spectrum despite the presence of hydrogen bridges, established by independent methods, for example, for the BHC with tetrahydroborate groups[53], $CH_2(C_5H_4)_2TiH_2AlH_2$,[41] and $(Cp_2Ti)_2AlH_4Cl$.[99] In the last case this is attributed to an intramolecular exchange interaction[99].

The correctness of the interpretation of the EPR spectrum can be readily (in most cases) checked by substituting the hydride hydrogen by deuterium. An increase in the number of components (J_2D = 1) [21,61] is then observed for the sodium- and magnesium-containing BHC of titanium(III) [for example, when $(C_5H_5)_2TiCl_2$ is replaced by $(C_5D_5)_2TiCl_2$, the reduction with sodionaphthalene gives rise to a 20-component multiplet instead of the 11-component multiplet[61]]. On the other hand, the HFS of Cp_2TiD_2AlXX' due to the nuclei is usually unresolved and the EPR spectrum shows a well-resolved sextet[39,51] (Table 1).

In some cases, it has proved possible to resolve the super-HFS of the EPR spectrum of Cp_2TiH_2M' due to the protons of the C_5H_5 groups (a_{HCp} = 0.2–0.6 G) and also the ^{47}Ti(J = 5/2) and ^{49}Ti(J = 7/2) nuclei, manifested as "satellites" at the edges of the spectrum.

The form and parameters of the EPR spectra of the isotypical BHC in inert and solvating solvents differ only slightly. Since the Lewis base is not removed on crystallisation of the BHC, there is no doubt that the latter are solvated also in solutions. One can therefore postulate that the molecules of the solvating solvent are not linked to the Ti atoms but are coordinated to the Al atom.

It follows from the data presented that all the BHC Cp_2TiH_2M', where M' = Li, Na, MgHal, or AlX_2, have in solution a structure of type (I) and (II) with two bridging H atoms occupying two equivalent orbitals of the Ti atom:



The non-transition metal atoms lie on the z axis of the Cp_2Ti fragment. The question of the orientation of the orbital occupied by the unpaired electron (on the z axis[40] or at right angles to it, as for the orbital with the unshared electron pair[100]) remains open.

Table 1. Parameters of the EPR spectra of bimetallic cyclopentadienyltitanium complexes.

Compound	Method of synthesis	Solvent	Factor	Form of signal (intensity)	a_H, G	$a_{M'}$, G	a_{Tl}, G	a_{HCp}, G	References
$Cp_2TiCl \cdot C_4H_8O$		THF	1,979	Singlet	—	—	—	—	[52]
$Cp_2TiCl_2Li(Na)$	I	Toluene	1,977	ditto	—	—	—	—	[52]
Cp_2TiCl_2MgBr	I	Et_2O	1,977	»	—	—	—	—	[52]
$Cp_2TiClBCl_2$	—	C_6H_6	1,975	Quartet (1:1:1:1)	—	5.8	—	—	[93]
$Cp_2TiCl_2AlCl_2$	I	C_6H_6	1,975	Sectet (1:1:1:1:1:1)	—	6.7	3.8	—	[47]
$CpTi(Cl_2AlCl_2)_2$	—	C_6H_6	1,972	11 Components	—	5.7	—	—	[94]
$(Cp_2Ti)_3AlCl_3$	—	C_6H_6	1,973	Sextet (1:1:1:1:1:1)	—	7.0	—	—	[64]
$Cp_2TiCl_2AlClMe$	I	C_6H_6	1,975	Unresolved sextet	—	3.7	—	—	[47]
$Cp_2TiCl_2AlClEt$	I	C_6H_6	1,975	ditto	—	3.2	—	—	[46, 47]
$Cp_2TiCl_2 \cdot AlEt_2$	I	C_6H_6	1,976	»	—	1.8	—	—	[47, 59]
Cp_2TiCl_2AlClH	IV	Oct-1-ene	1,979	Sextet	—	4.0	—	—	[33]
$Cp_2TiH \cdot C_4H_8O$	II	THF		Doublet	11.6	—	—	—	[31]
$Cp_2TiHClLi$	II	Toluene	1,983	ditto	7.0	—	—	—	[52]
$Cp_2TiHClNa$	II	THF	1,983	»	9.1	—	—	—	[52]
$Cp_2TiHClMgBr$	II	Et_2O	1,984	»	3.6	—	—	—	[52]
$Cp_2TiHClAlEt_2$	I, II	Toluene	1,985	ditto	6.3	—	—	—	[43, 44]
Cp_2TiH_2Li	II	Et_2O	1,992	Multiplet	9.5	2.9	—	—	[52, 95]
Cp_2TiH_2Li	I	Et_2O	1,992	Triplet	8	—	—	—	[58]
Cp_2TiH_2Li	III	THF	1,994	Triplet of quartets	9.8	2.3	—	0.27	[60]
Cp_2TiH_2Na	II	THF	1,993	Multiplet	10.1	6.9	—	—	[52]
Cp_2TiH_2Na	III	THF	1,994	»	9.8	6.7	7.2	—	[40, 60]
Cp_2TiH_2MgBr	I, II	Et_2O	1,993	Triplet (1:2:1)	7.8—8.1	—	7.4	0.39	[21, 52, 40]
Cp_2TiH_2MgI	III	THF	1,994	ditto	7.9	—	—	—	[61]
Cp_2TiD_2MgBr	I	Et_2O	1,993	Quintet (1:2:3:2:1)	2.4	—	—	—	[21]
$Cp_2TiH_2AlMe_2$	IV	Toluene	1,992	Multiplet	4.65	6.9	—	0.3	[48, 49]
$Cp_2TiH_2AlEt_2$	I	»	1,987	Octet (1:3:4:4:4:4:3:1)	3.9	3.9	—	41	[47]
$Cp_2TiH_2Al(iso\text{-}Bu)_2$	IV	»	1,988	ditto	4	4	—	—	[42, 43]
$Cp_2TiH_2AlH_2$	IV	THF Et_2O	1,991	«	5.5	5.5	4.0	0.48	[39, 40]
$CH_2(C_5H_4)_2TiH_2AlH_2$	V	Et_2O	1,989	Singlet					
Cp_2TiH_2AlHBr	IV	Et_2O	1,989	13-Component multiplet (1:2:2:2:2:2:2:2:2:2:2:2:1)	— 3.8	— 7.6	—	—	[41] [51]
$(Cp_2TiH_2AlHCl)_2$	IV	Et_2O	1,989	17-Component multiplet	6.5 29.5	3.5	—	—	[37, 51, 96]
$Cp_2TiH_2AlCl_2$	III	THF	1,993	Sextet of triplets	3.1	10.8	—	0.57	[63, 64]
$Cp_2TiH_2AlCl_2$	IV	2-Methyl-THF Et_2O	1,992	ditto »	3.0 3.3	10.5 10.1	5.4 —	0.50 —	[40] [51]
$Cp_2TiH_2AlBr_2$	IV	Et_2O		»	3.4	10.0	—	—	[51]
$(Cp_2Ti)_2AlH_4Cl$	IV	Et_2O	1,989	Singlet	—	—	—	—	[99]
$Cp(Cl)TiH_2MgI$	III	THF	1,994	Triplet (1:2:1)	8.0	—	—	—	[53]
$[Cp_2VH_2AlEt_2]^+$	I	Toluene	1,990	Octet of octets	3.3	3.3	65	—	[47]
$Cp_2V(Cl)Cl_2AlCl_2$	I	CH_2Cl_2	1,968	Octet	—	—	73.9	—	[97]
$Cp_2V(H)Cl_2AlEt_2$	I	Pentane	1,996	Octet of doublets	5.7	—	41.1	1.6	[98]

It has also been suggested[63] that the TiH_2Al bridge may be asymmetric, as in the molybdenum complexes $[Cp_2MoH_2CuI]_2$.[101] The greatest strength of the hydride bridges compared with other types of bonding is consistent with the increase of the spin density of the unpaired electron at the aluminium atom in the sequence $Cp_2TiCl_2AlR_2 < Cp_2TiHClAlR_2 < Cp_2TiH_2 \cdot AlR_2$.[43,46,47] The amount of ionic character of the compounds increases in the sequence $M' = AlH_2 < AlCl_2 < MgBr < Li < Na$, which should apparently lead to an increase of the H–Ti–H angle[40].

One must note that the successive replacement of the terminal atoms in $Cp_2TiX_2AlX'_2$ by more electron-accepting ligands leads to a linear increase of the HFC constants a_{Al} and to a decrease of a_H for the BHC, the constants being linked by the simple relations $a_H = a_{Al}$ for $X = X' = H$,[38,39,51] Et,[44] or iso-Bu,[43] $a_H = \frac{2}{3}a_{Al}$ for $X' = X = Me$,[48,49] $a_H = \frac{1}{2}a_{Al}$ for $X = H$ and $X' = Br$,[51] and $a_H = \frac{1}{3}a_{Al}$ for $X = X' = Cl$[49,58,90] or Br.[51] The linear variation of properties such as the dipole moment μ and the standard enthalpy of formation ΔH_f^0 with increasing n was noted previously for $AlH_nCl_{3-n} \cdot L$,[102,103] where $n = 0$ and 3 and $L = NR_3$, Et_2O or THF.

Very few BHC of this type have been isolated in a pure state, although the alkyl derivatives $Cp_2TiX_2AlR_2$, where $X = Cl$ or Me,[104] and the complexes $Cp_2LnR_2AlR_2$ with similar properties, where Ln = Y, Yb, Sc, or Ho, are known[105]. The isolation of $Cp_2TiH_2Al(iso\text{-}Bu)_2$ in the form of a red-violet oily substance[40] has been reported but none of its characteristics are quoted in the above communication.

When an excess of $AlEt_3$ was allowed to act on Cp_2TiCl_2[104,106] or on Cp_2TiPh_2 and Cp_2TiCl,[17] a red diamagnetic substance was obtained, melting without decomposition at 169–191 °C and readily soluble in water and hydrocarbons. It has been established by X-ray diffraction that in this compound the titanium and aluminium atoms are linked by hydrogen bridges and the compound is described by the formula $[Cp(C_5H_4) \cdot TiHAlEt_2]_2$.[17] A further two compounds are formed on

treating the "stable titanocene" with triethylaluminium. BHC with the compositions $[(CpTi)_2H.(H_2AlEt_2)](C_{10}H_8)$ and $[(C_5H_4)TiHAlEt_2]_2(C_{10}H_8)$ crystallise at 20° and 100 °C respectively[54]. Analogous compounds are also formed when $AlEt_3$ is replaced by $AlMe_3$.[107]

"Zirconocene" reacts in a more complex manner and the composition of the products of the addition of $AlEt_3$ to it has not therefore been established[107].

The structures of the BHC considered (Fig.1) are derivatives of two types of structures: the structure of "niobocene" containing π,σ-linked $\eta^5:\eta^1$-C_5H_4 groups (III) and the structure of "titanocene" containing the fulvalene ligand $\eta^5:\eta^5$-$C_{10}H_8$ (V). In the BHC (IV) the features of both types of structures are observed. The close relation between "titanocene" and the BHC obtained from it is also indicated by the finding that they are formed with a high yield on treating compounds (V) with an equivalent of water[54]. The Ti–Ti distance in these compounds (2.91–3.37 Å) is significantly greater than the sum of the covalent radii (2.72 Å), which indicates the absence of a direct metal–metal bond [with the possible exception of compounds (IV)]. Consequently, the titanium in these compounds is in the +3 oxidation state. The diamagnetism of the BHC considered is evidently of the same type as in "titanocene" and its derivatives[108]. The Al–C and Ti–C distances are close to the sums of the covalent radii (1.95 Å and 2.13 Å), i.e. the Ti–C_{ring}–Al bond can apparently be described as a three-centre bond analogous to, for example, the Al–C–Al bond in Al_2Me_6.

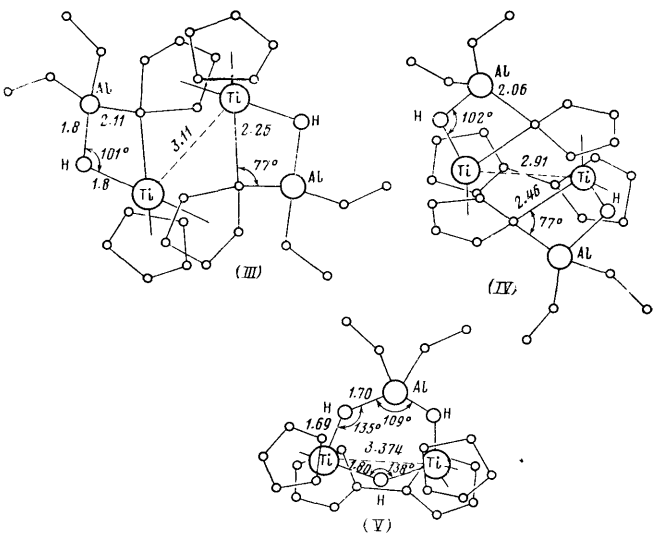
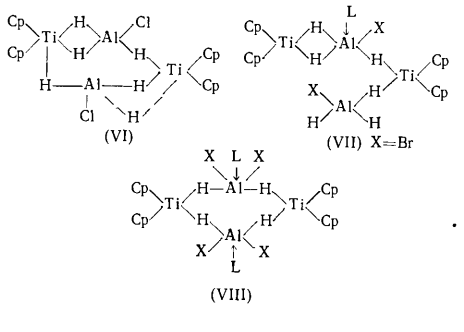


Figure 1. The structures of the bimetallic hydride complexes $[Cp(C_5H_4)TiHAlEt_2]_2$ (III), $(C_{10}H_8)[(C_5H_4)TiHAlEt_2]_2$ (IV), and $(C_{10}H_8)[Cp_2Ti_2(H)(H_2AlEt_2)]$ (V) according to X-ray diffraction data[17,54].

The ^1H NMR data for these compounds agree well with the results of X-ray diffraction analysis (Fig.1). The chemical shift of the protons in the Ti–H–Al bridge is in the range 16.6τ–21.6τ, whereas the chemical shift of the protons in the homonuclear Ti–H–Ti bridge is significantly greater and equal to 31.8τ.[17,54]

The interaction of zinc aryls and alkyls with titanium(IV) biscyclopentadienylalkyls (or the corresponding aryls) and the "metastable titanocene" leads to the formation of the diamagnetic complexes $(C_{10}H_8)(C_5H_4)(C_5H_3R)Ti_2(H)(R')Zn$, where R = H or Ph and R′ = Ph or Me.[109] The presence of the metal–hydrogen bond is confirmed by the formation of HD in the reaction with DCl, although the ν(Ti–H) bands were not observed in the infrared spectra. Structural formulae incorporating bridge or terminal Ti–H and Ti–R bonds and a dicoordinate zinc atom have been proposed for these compounds[109]. We believe that these formulae are unlikely bearing in mind the fact that the compounds are non-solvated. The "stable titanocene", which has two bridging hydrogen atoms[110], decomposes $ZnPh_2$ to metallic zinc and benzene, evidently as a result of the decrease of the stability of the complex on passing from the alkyl hydride to zinc hydride[109].

When the complexes $Cp_2TiAlH_nHal_{4-n}.L$ (n = 2–4, L = NEt_3 or OEt_2) are isolated from solutions, rearrangements take place and are in some cases accompanied by the loss of hydrogen (n = 4).[104] The structure (II) persists apparently only for $Cp_2TiH_2AlHal_2.NEt_3$.[111] The compounds obtained contain 0.5 or 1 (n = 2) mole of a Lewis base per gram atom of titanium and are paramagnetic intensely coloured substances moderately soluble in ethyl ether and benzene and extremely sensitive to oxidation and hydrolysis[111,112]. Infrared spectroscopic study of these compounds revealed the presence of three groups of ν(M–H) absorption bands, one of which was assigned to the vibrations of the terminal Al–H bonds (1750–1900 cm^{-1}) and the other two to vibrations of different types of hydrogen bridges, apparently the double TiH_2Al bridges (1150–1260 cm^{-1}) and the single TiHal bridges (1350–1500 cm^{-1}).[111] The halogen atoms are in all cases terminal[111]. The tendency towards rearrangements diminishes with decrease of n, on replacement of Cl by Br and of OEt_2 by NEt_3, and also on reducing the temperature of the synthesis. $Cp_2TiAlH_3.0.5OEt_2$ apparently contains $\eta^1:\eta^5$-C_5H_4 groups and its structure resembles structure (III). The structural formulae (VI)–(VIII) have been proposed[111] for the compounds $Cp_2TiAlH_3.OEt_2$ and $Cp_2TiAlH_2Hal.OEt_2$ on the basis of EPR and infrared spectroscopic data[51,111], as well as CT data[37,51]. The authors[111] do not rule out the possibility of the dimerisation of compounds (VI)–(VIII) via bridging $\eta^5:\eta^1$-C_5H_4 groups, as in the study of Tebbe and Guggenberger[17]:



On crystallisation of $Cp_2TiAlH_nCl_{4-n}.L$ with n = 0 and 1, only Ti : Al = 3 : 1 complexes with chloride bridges mixed with the solvates $AlCl_3.L$ (n = 0) or complexes of unknown composition with AlHCl.L (n = 1) were detected in the solid phase by infrared spectroscopy[89]. The compounds $Cp_2TiH_{2-n}.AlX_{2+n}$ are formed as intermediates also in the more complex reaction involving the reduction of Cp_2TiCl_2 by lithium tetrahydroaluminate[37]. According to EPR and CT data, the reaction then proceeds via a series of intermediate stages[34–37]

and terminates with formation of the unstable compound $Cp_2TiH_2.AlH_2.AlH_3$, which decomposes in accordance with Eqn.(38):

$$Cp_2TiCl_2 + LiAlH_4 \rightarrow [Cp_2TiH_2AlCl_2 \cdot Cp_2TiCl] + LiCl + H_2 \; ; \quad (34)$$

$$Cp_2TiH_2AlCl_2Cp_2TiCl + LiAlH_4 \rightarrow [Cp_2TiH_2AlH(Cl)]_2 \; ; \quad (35)$$

$$[Cp_2TiH_2AlHCl]_2 + LiAlH_4 \rightarrow [Cp_2TiH_2]_2\,Al_2H_3Cl + AlH_3 + LiCl \; ; \quad (36)$$

$$[Cp_2TiH_2]_2\,Al_2H_3Cl + AlH_3 + LiAlH_4 \rightarrow 2Cp_2TiH_2AlH_2 \cdot AlH_3 + LiCl \; ; \quad (37)$$

$$Cp_2TiH_2AlH_2 \cdot AlH_3 \rightarrow Cp_2TiH_2AlH_2 + Al + \tfrac{3}{2}H_2 \; . \quad (38)$$

Isagawa et al.[113] believe that the final product of these reactions is the complex $Cp_2Ti(AlH_3)_2$, but they do not take into account the instability of the entire system with respect to decomposition reaction and $Cp_2Ti(AlH_3)_2$ can therefore be regarded also as a partly decomposed form of $Cp_2TiH_2AlH_2.AlH_3$.

In contrast to the titanium compounds, the BHC of zirconium(IV) and hafnium(IV) are not reduced by complex hydrides, so that only BHC containing the metal in the +4 oxidation state (mainly zirconium) have been described in the literature, although one can assume that in the future zirconium compounds analogous to the titanium(III) BHC examined above will be obtained (for example, on the basis of "zirconocene" isomorphous with the stable "titanocene"), namely $(C_{10}H_8)(CpTiH)_2$.[114]

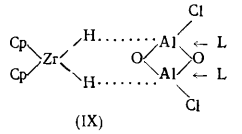
Biscyclopentadienylzirconium(IV) hydride tetrahydroaluminate has been obtained by the exchange reaction[115]

$$[Cp_2Zr(H)Cl]_x + x\,LiAlH_4 \xrightarrow{THF,\,C_6H_6} [Cp_2Zr(H)AlH_4]_x + x\,LiCl \; . \quad (39)$$

The solubility of the compound thus obtained is higher than that of the polymeric zirconium hydride complexes $[Cp_2Zr(H)X]_x$, where X = Cl or Me,[115] which may indicate a lower degree of association of the tetrahydroaluminate.

The reaction of $LiAlH_4$ with $(Cp_2ZrCl)_2O$ [Eqn.(40)], which terminates with the formation of the polymeric $(Cp_2ZrCl)_2O$,[115] may proceed via a stage involving the formation of the unstable complex (IX), decomposing on crystallisation:

$$(Cp_2ZrCl)_2O + LiAlH_4 \rightarrow 2/x\,[Cp_2ZrH_2]_x + LiCl + 1/2\,\{AlOCl\} \; ; \quad (40)$$

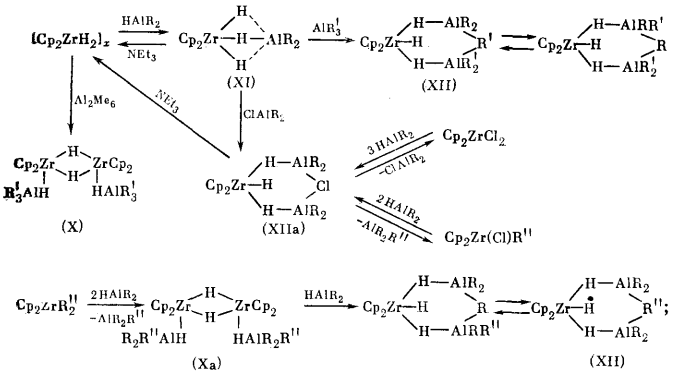


(IX)

The interaction of $(Cp_2ZrH_2)_x$ with Al_2Me_6 [26] leads to the formation of the molecular dimeric adduct $[Cp_2ZrH_2AlMe_3]_2$, which is fairly soluble in benzene. The adducts of $[Cp_2Zr.(H)Cl]_x$ with Al_2Me_6 are much less stable[26].

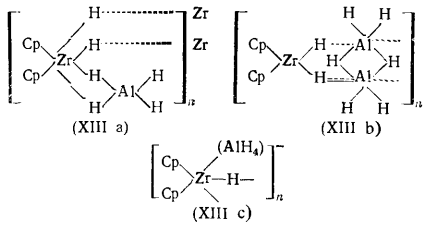
Several BHC of zirconium have been isolated in the form of pale-blue or pale-violet oily substances on treatment of biscyclopentadienyl compounds of zirconium(IV) with di-isobutylaluminium hydride[32]. The BHC of zirconium obtained were identified and their structure postulated on the basis of measurements of molecular weights and NMR data (Scheme 1):[26,32,115]

Scheme 1



R = t-Bu, R′ = Me, R″ = neohexyl.

Two models of the structure of biscyclopentadienylzirconium hydride tetrahydroaluminate have been proposed[115]: the bridged tetrahydroaluminate (XIIIa) (bidentate AlH_4 group) and the adduct with aluminium hydride (XIIIb):



(XIII a) (XIII b)

(XIII c)

The model (XIIIb) is inconsistent with the frequency ν(Al–H) (1790, 1700 cm^{-1}), which is characteristic of a tetracoordinate and not hexacoordinate aluminium atom[116]. Bearing in mind the method of synthesis of $[Cp_2Zr(H)AlH_4]_x$,[115] one can postulate that the polymeric skeleton of $[Cp_2Zr(H)Cl]_x$ persists [the frequencies ν(Zr–H–Zr) are respectively 1425 and 1390 cm^{-1}]. Since the bidentate AlH_4 group is a four-electron ligand like the BH_4 group[117], the zirconium atom in compound (XIIIa) has formally a 20-electron configuration. On the other hand, its tetrahydroborate analogue $Cp_2Zr(H)BH_4$ is monomeric and has an 18-electron configuration[25]. Although the 20-electron complexes of zirconium and hafnium are known, for example, $Cp_2Hf(BH_4)_2$ [118] and Cp_3ZrH,[119] it is also necessary to consider the 18-electron analogue (XIIIa) with a monodentate or ionic AlH_4 group, as in model (XIIIc). This is also indicated by the absence of the ν(Zr–H–Al) absorption bands in the range 1100–1500 cm^{-1},[26,115] which are characteristic covalent titanium tetrahydroaluminates[111].

The signal of the methyl protons in $(Cp_2ZrH_2AlMe_3)_2$ (0.41τ) is displaced downfield relative to Al_2Me_6 as a consequence of the formation of the Al–H bond[26]. The frequency of ν(Al–H) in the spectrum of the BHC (1780 cm^{-1}) corresponds to a tetracoordinate Al atom[116] and H in the terminal position. NMR data show that the CH_3 groups are also terminal[26]. Consequently, the zirconium atoms in both $[Cp_2Zr(H)AlH_4]_x$ and $[Cp_2ZrH_2AlMe_3]_2$ are linked by two hydride bridges and each is joined to the $AlHMe_3$ or $(AlH_4)^-$ group by an ionic bond, as in (XIVb).

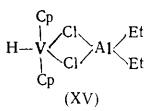
The butyl complex $(Cp_2ZrH_2Al(iso\text{-}Bu)_2C_6H_{13})_2$ evidently has a structure analogous to (Xa).

The chemical shift of the hydride protons in compounds (X)–(XII) (10.3τ–11.2τ for Zr–H and 12.0τ–12.9τ for Zr–H–Al) hardly changes, i.e. the nature of the Zr–Al bond is probably the same in all the complexes. The NMR data are satisfactorily consistent with the structural formulae (X) to (XII),[32] (Scheme 1) in which the zirconium atoms are coordination saturated.

The zirconium tetrahydroaluminate complexes are thermally unstable and decompose at room temperature[26,32], while $[Cp_2Zr(H)AlH_4]_x$ decompose above 60 °C in solution[107]. The main gaseous decomposition product of the latter is hydrogen, while in the case of $[Cp_2Zr(D)AlD_4]_x$ almost pure HD is formed[107]. According to infrared spectroscopic data, the Zr–H–Zr linkages are then retained, while the ν(Al–H) vibrations disappear. Consequently the tetrahydroaluminate and cyclopentadienyl groups participate in the elimination of H_2 and an $Al–C_5H_4$ σ-bond is then formed, as in the case of $[Cp(C_5H_4)TiHAlEt_2]_2$.[17] Hydrogen and methane are evolved on decomposition of $[Cp_2ZrH_2AlMe_3]_2$, but the Cp groups are apparently not involved[26].

2. Group VA

The biscyclopentadienyl BHC of vanadium are almost unknown. In the study of the $Cp_2VCl_2–AlH(iso\text{-}Bu)_2$ system by EPR, it was noted that, after the introduction of a small amount of oxygen to the system containing reduced vanadium, an eight-component EPR signal appears with broadened (ΔH = 30 G) lines[44]. The authors explained the broadening by the presence of an unresolved HFS associated with the splitting by two protons and the aluminium atom (as in the $Cp_2TiH_2AlR_2$ complexes[40,42–44]) and the EPR signal is attributed to the complex $Cp_2VH_2Al(iso\text{-}Bu)_2$, i.e. one can assume that BHC having the compositions $Cp_2VHClAl(iso\text{-}Bu)_2$ and $Cp_2VH_2Al(iso\text{-}Bu)_2$ with structure (I) are formed in the $Cp_2VCl_2–AlH(iso\text{-}Bu)_2$ system. BHC are also formed in the $Cp_2VCl_2–Et_2AlCl$ system in an amount of approximately 10% of the initial Cp_2VCl_2 concentration. Differentiation of the EPR spectrum showed that each line of the octet ($J_{^{51}V}$ = 7/2) with a_V = 41.1 G is split into a doublet (a = 5.7 G), which may be due to the interaction of the unpaired electron of vanadium(IV) with a proton[98]. The following structural formula was attributed[88] to the BHC observed on the basis of data for the anisotropic splitting:



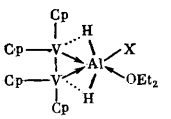
(XV)

The physical and physicochemical properties of biscyclopentadienylvanadium(III) tetrahydroborate Cp_2VBH_4 are very close to those of Cp_2TiBH_4, although the former compound is less stable[121]. The tetrahydroaluminate complexes obtained by the reaction of Cp_2VCl with lithium tetrahydroaluminate in diethyl ether are also less stable in solution[122]. The reaction proceeds in two stages: the first stage proceeds up to the ratio $Cp_2VCl : LiAlH_4 = 2 : 1$ and involves a heat change of 126.7 kJ mol^{-1}, which is close to the heat of the analogous reaction involving Cp_2TiCl (140 kJ mol^{-1}),[37] while the second stage, leading to the complete removal of chlorine from solution, is not accompanied by the evolution of heat.

The evolution of 0.5 mole of H_2 per mole of Cp_2VCl in the first stage indicates the reduction of vanadium(III) to vanadium(II). It has been suggested[122] that the vanadocene formed gives rise to a diamagnetic complex with monochloroalane:

$$2Cp_2VCl + LiAlH_4 \xrightarrow{Et_2O} (Cp_2V)_2AlH_2Cl + LiCl + H_2 . \quad (41)$$

According to infrared spectroscopic data, this substance contains bridging hydrogen atoms and a terminal chlorine atom [$\nu(Al–Cl_{term})$ = 440 cm^{-1}] and has the composition $(Cp_2V)_2AlH_2Cl.OEt_2$. The structural formula (XVIa) has been proposed for this substance. The unstable complex (XVIb) with aluminium hydride is apparently formed in the second stage of the reaction:



(XVII)

(a) X=Cl;

(b) X=H.

A series of BHC are known for niobium(III) and niobium(IV), these being formed on interaction of aluminium, gallium, and zinc alkyls with biscyclopentadienylniobium and biscyclopentadienyltantalum hydrides[123]:

$$Cp_2TaH_3 + MEt_n \underset{20°}{\overset{C_6H_6}{\rightleftharpoons}} Cp_2Ta(H)_2HMEt_n,\ M=Al,\ Ga,\ Zn,\ Cd ; \quad (42)$$

$$Cp_2NbH_3 + AlEt_3 \underset{-50°}{\overset{C_6H_5CH_3}{\rightleftharpoons}} Cp_2Nb(H)_2HAlEt_3 ; \quad (43)$$

$$Cp_2Nb(L)H + AlEt_3 \xrightarrow{20°,\ C_6H_6} Cp_2Nb(L)HAlEt_3,\ L=C_2H_4,\ CO,\ PMe_3 ; \quad (44)$$

$$[Cp(C_5H_4)NbH]_2 + 2AlEt_3 \xrightarrow{20°,C_6H_6} [Cp(C_5H_4)NbHAlEt_3]_2 . \quad (45)$$

The BHC have been isolated in a crystalline form. They are readily soluble in benzene, which made it possible to demonstrate the correspondence between the molecular weights and the proposed formulae, decompose in the light at room temperature, and are stable in the dark in the course of a week. The complexes with gallium, zinc, and cadmium alkyls are less stable and exist in equilibrium with the initial compounds only in solution; on crystallisation, equilibrium (42) shifts to the left. In contrast to tantalum, niobium(V) is reduced by metal alkyls and the adducts $Cp_2NbH_3.MEt_n$ have been detected by NMR only between −40° and −50 °C, splitting off alkanes on raising the temperature and giving rise to the BHC of niobium(III):[56]

$$Cp_2Nb(H_2)HAlEt_3 \xrightarrow{C_6H_6} Cp_2NbH_2AlEt_2 + C_2H_6 ; \quad (46)$$

$$2Cp_2Nb(H_2)HZnEt_2 \xrightarrow{C_6H_6} (Cp_2NbH_2)_2Zn + ZnEt_2 + C_2H_6 . \quad (47)$$

The BHC of this type are also formed on interaction of Cp_2NbCl_2 with $Na(Li)AlH_4$ and its derivatives $NaAlH_2X_2$ (X = Et or $OCH_2CH_2OCH_3$) [reaction (47)].[20] The reaction may proceed via a stage involving the disproportionation of the unstable niobium(IV) hydride[20]:

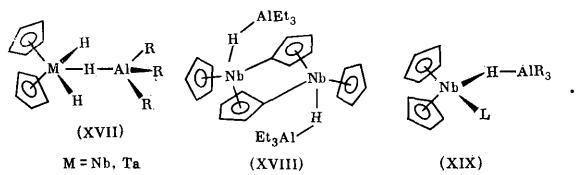
$$Cp_2NbCl_2 + NaAlH_2X_2 \xrightarrow{C_6H_6,\ THF} \begin{matrix} Cp_2NbH_2 + HAlX_2 + NaCl \\ \downarrow \qquad\quad \downarrow \\ Cp_2NbH_3\ \ Cp_2NbH \quad AlHX_2 \end{matrix} \rightarrow Cp_2NbH_2AlX_2 . \quad (48)$$

The interaction between Cp_2TaCl_2 and $NaAlH_2(OCH_2CH_2.OCH_3)_2$ proceeds analogously[124]. Although the intermediates have not been isolated, hydrolysis results, as in the study of Labinger and Quai Sam Wong,[20] in a satisfactory yield of Cp_2TaH_3.[124] In contrast to the tetrahydroborate Cp_2NbBH_4, the compounds $Cp_2NbH_2AlX_2$ do not react with

PR_3, CO, and C_2H_4 and do not form the complexes $Cp_2Nb.(H)L$.[20] The signal due to the hydride hydrogen atoms gradually appears in the benzene solution of $Cp_2NbD_2AlD_2$, which has been explained by the H/D exchange between the C_5H_5 rings and the AlD_4^- group. Only the bridging hydrogen atoms are exchanged and in THF the exchange is retarded evidently owing to the blocking of the coordination site by the solvent.

Treatment of a solution of Cp_2TaH_3 in toluene with LiBu [124] give rise to an insoluble orange substance containing, together with Ta–H bonds, apparently also Ta–Li bonds and having chemical properties resembling those of the BHC $[Cp_2Mo(H)Li]_4$ (see subsection 3 below).

The coordination of a non-transition metal alkyl or hydride leads to an upfield shift of the hydride proton signal by 3–7 p.p.m. and to a bathochromic shift of ν(M–H) (Table 2). In the case of the coordination-saturated trihydrides Cp_2MH_3 the shift is selective, i.e. mainly the signal of the central proton A (in the AB_2 system) is displaced[20,124]. Consequently, the structure of the BCH with the composition $Cp_2MH_3.AlR_3$ can be described by the structural formula (XVII) incorporating a single M–H–Al hydrogen bridge. Single hydrogen bridges are evidently present also in the BHC based on the "niobocene" (XVIII) and the hydrides $Cp_2Nb(L)H$ (XIX),[123] whereas structures with double hydrogen bridges of type (I) are more likely in the complexes of Cp_2NbH with aluminium and zinc hydrides[20,123]. This has been confirmed by NMR data, which have been satisfactorily interpreted on the hypothesis that the non-transition metal atom is located on the symmetry axis *z* of the Cp_2NbH_2 fragment[123].



(XVII) M = Nb, Ta (XVIII) (XIX)

Table 2. ^1H NMR and infrared spectroscopic data for the biscyclopentadienyl BHC of vanadium, niobium, and tantalum.

Compound	ν (M–H), cm^{-1}	$\tau_{C_5H_5}$	τ_{MH}	$\Delta\tau_{M-H}$	References
$(Cp_2V)_2AlH_2Cl\cdot OEt_2$	1575	—	—	—	[122]
$Cp_2Nb(H_2)\cdot AlHEt_2$	—	5.12	15.0 (A) 14.5 (B_2)	+2.4 +1.0	[20]
$Cp_2Nb(PMe_3)HAlEt_3$	—	—	23.12	+5.28	[123]
$Cp_2Nb(C_2H_4)HAlEt_3$	—	—	19.63	+6.68	[123]
$Cp_2Nb(CO)HAlEt_3$	—	—	21.51	+5.12	[123]
$Cp_2Nb(CO)HZn(BH_4)_2$	1400	—	—	—	[125]
$Cp_2Nb(CO)HFe(CO)_4$	1720	—	16.4	−0.1	[126]
$Cp_2Nb(H)(\mu\text{-}C_5H_4)Fe(CO)_2$	1780	—	—	—	[127]
$Cp_2NbH_2AlEt_2$	—	—	22.78	+9.0 *	[123]
$Cp_2NbH_2AlEt_2$	—	5.37	21.4	+7.9 *	[20]
$Cp_2NbH_2Al(OCH_2CH_2OCH_3)_2$	—	5.40	20.2	+6.7 *	[20]
$Cp_2NbH_2AlH_2$	1680 **	5.15	19.8	+6.3 *	[20]
$(Cp_2NbH_2)_2Zn$	—	—	19.05	+5.32 *	[123]
$[(C_5H_4)CpNbHAlEt_3]_2$	—	—	17.02	+4.95	[123]
$Cp_2Ta(H_2)HAlEt_3$	—	—	14.68 (A) 1.46 (B_2)	+3.05 −0.57	[123]
$[Cp_2TaH_{3-n}Li_n]$	1590 ***	—			[124]

*Relative to the signals of the H_2 protons in Cp_2NbH_3.
**The centre of a broad band with shoulders.
***The centre of a broad band.

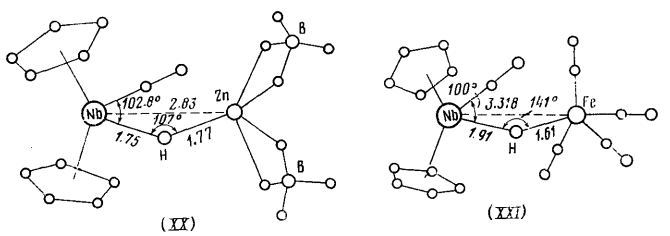
The reduction of "niobocene" with sodium naphthalide yielded the red anionic complex $Na_2[CpNb(\eta^1:\eta^5\text{-}C_5H_4)H]_2$.[128] An analogous complex containing cyclopentadienyl rings linked via a siloxane bridge has been obtained by the reduction of $[C_5H_4Si(Me_2)OSi(Me_2)C_5H_4]NbCl_2$ with sodium in toluene and subsequent treatment with diethyl ether. According to X-ray diffraction data, it retains the geometry of "niobocene" with isolated sodium ions solvated by two diethyl ether molecules. The Nb–Nb distance then increases (to 3.93 Å) and the Nb–H distance decreases together with an increase of the ν(Nb–H) frequency.

In the BHC of niobium(III) having an unshared electron pair, there is a possibility of the formation, in addition to the Nb–H–Al bridge bonds, also of a direct Nb → Al donor–acceptor bond. Indeed, according to the X-ray diffraction data for the unusual BHC $Cp_2Nb(CO)HZn(BH_4)_2.0.5C_6H_6$, obtained in accordance with Eqn.(4),[120,125,129] the niobium atom in this compound is linked to the electron-deficient molecule of zinc tetrahydroborate via both the Zn–H–Nb hydrogen bridge and the direct Nb–Zn bond (the Nb–Zn distance is close to the estimated sum of the covalent radii, namely 2.7 Å) (Fig.2). The stretching vibration frequency of the metal–hydrogen bond in compound (XX) undergoes a bathochromic shift on complex formation by ~350 cm^{-1}:[125]

$$NbCl_5 + CpNa + Zn \xrightarrow{THF,\,CO} \{Cp_2Nb(CO)ZnCl_2\} \xrightarrow{NaBH_4} Cp_2Nb(CO)HZn(BH_4)_2 \quad (49)$$

(XX)

An analogous complex containing niobium and iron and having the composition $Cp_2Nb(CO)HFe(CO)_4$ (XXI) has been obtained on treatment of Cp_2NbH_3 with $Fe(CO)_5$.[130] In view of the short metal–hydrogen bond distances (Fig.2), the authors postulate the presence of the Nb–H–Fe linkages and not of the direct Nb–Fe bond. The similarity of the spectroscopic characteristics of the Nb–H bond in $Cp_2Nb(CO)HFe(CO)_4$ to the analogous parameters in the monomeric $Cp_2Nb(CO)H$ (Table 2) and also the application of the 18 electron rule indicate a low probability of the existence of the Nb–H–Fe bridge. A terminal Nb–H bond has been postulated in the complex $Cp_2Nb(H)(\eta\text{-}C_5H_4)Fe(CO)_2$.[127]



(XX) (XXI)

Figure 2. The molecular structures of $Cp_2Nb(CO)HZn(BH_4)_2$ (XX) [129] and $Cp_2Nb(CO)HFe(CO)_4$ (XXI).[130]

3. Groups VIA and VII

As a consequence of the filling of all the unoccupied orbitals by the unshared electron pairs on formation of the metal–hydrogen bond, the biscyclopentadienyl derivatives of Group VIA (Mo, W) and VIIA (Te, Re) metal hydrides are bases and readily form 1 : 1 adducts with Lewis acids (H^+, boron and aluminium alkyl and halides, transition metal salts, etc.).

The adducts of magnesium and transition metal compounds with the halides of boron (diborane and BMe_3 do not react) and aluminium are almost insoluble in diethyl ether and aromatic hydrocarbons. The complexes with transition metals are

soluble in THF, dimethyl sulphoxide (DMSO), dimethylformamide (DMF), and pyridine[30] and those with aluminium alkyls are soluble also in aromatic hydrocarbons[27,82,131]. According to cryoscopic data, the latter are monomeric in solution[27]. As in the protonation reaction[126,132], Cp_2ReH combines with only one molecule of the Lewis acid[28,133].

The unstable adduct $Cp_2WH_2.AlH_3$ is apparently formed on interaction of Cp_2WH_2 and aluminium hydride[27], but all attempts to isolate it as well as the complex $Cp_2WH_2.AlHMe_2$ were unsuccessful. The reaction does not proceed at all with gallium hydride, although $GaMe_3$ gives rise to an unstable adduct[131].

The more stable complexes of Cp_2MoH_2 with aluminium halides and dihalogenoalanes have been obtained by the reaction[24]

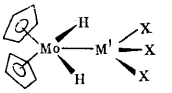
$$Cp_2MoH_2 + AlHal_{3-n}H_n \cdot OEt_2 \rightleftarrows Cp_2MoH_2 \cdot AlHal_{3-n}H_n + Et_2O,\ n = 0, 1. \quad (50)$$

Reaction (50) has been investigated in solvents with different solvating capacities and it has been concluded that the basicity of Cp_2MoH_2 exceeds only slightly that of diethyl ether[24]. The earlier view that the basicities of Cp_2MoH_2 and pyridine are comparable[82] is apparently wrong.

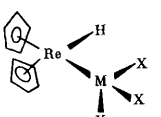
The equilibrium in the reaction of Cp_2MH_2 with transition metal compounds is fully displaced to the right, which can be accounted for either by the greater acidity of these compounds or by the formation of a different type of bond between the components.

These adducts as a rule crystallise from solutions in strongly solvated solvents in the form of the monosolvates $Cp_2MH_2.M'X_n.L$.[29,30,134–136]

The spectroscopic characteristics of the M–H bonds in the adducts $Cp_2MH_2.M'X_n$ are presented in Table 3. It follows from these data that the parameters of the metal–hydrogen bond hardly change on formation of adducts with compounds of Group IIIA elements. The chemical shift of the methyl protons (there is a downfield shift[26]), in $Cp_2MH_2.AlMe_3$ and the frequencies ν(B–Hal) in the complexes with $BHal_3$ correspond to tetracoordinate aluminium and boron atoms[27,28]. Hence it follows that in the adducts obtained the transition metal has two terminal hydrogen atoms and is linked to the non-transition element (B and Al) by a direct donor–acceptor bond (BHC of the fourth type):



(XXIIa)



(XXIIb)

A bathochromic shift of ν(Al–H) has been observed for the complexes of Cp_2MoH_2 with dihalogenoalanes[24] (Table 3) and is apparently associated either with a change in the C.N. of aluminium to 5 (the halogen bridge bond) or, what is more likely, with a significant decrease of the strength of the Al–H bond.

The adducts of $Cp_2Mo(W)H_2$ with aluminium alkyls are thermally unstable and gradually decompose in solution with liberation of alkanes and precipitation of solid products. As was to be expected, tungsten compounds are more stable than molybdenum compounds and the methyl complexes are more stable than the ethyl complexes[132].

The decomposition of $Cp_2WH_2.AlMe_3$ can proceed simultaneously via two pathways: the elimination of hydrogen from the Cp group formation of an Al–C σ-bond, and the elimination of the hydride hydrogen atom from tungsten with formation of a direct W–Al bond[132]. These reactions are common to strong alkylating agents—aluminium and lithium alkyls and Grignard reagents.

When the reaction between Cp_2MoH_2 and Al_2Me_6 is carried out in toluene at 80 °C, the orange crystals of the compound $C_{25}H_{35}Al_3Mo_2$ (XXIIIa) are formed[137]. Cp_2WH_2 reacts similarly, giving rise to the yellow crystals of $C_{25}H_{35}Al_3W_2$, which, however, is not isomorphous with the molybdenum compound[138]. Prolonged refluxing of the reagents makes it possible to obtain the yellow crystals of the compound $C_{26}H_{34}Al_4Mo_2$ (XXIIIb) (Scheme 2)[137].

Scheme 2

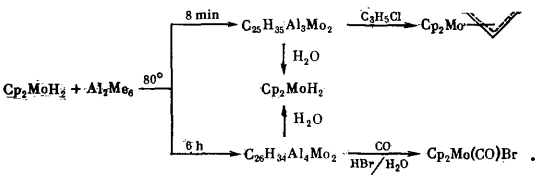


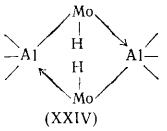
Table 3. The changes in the spectroscopic characteristics of the M–H bond on formation of complexes by Cp_2MH_2 (M = Mo or W) with Lewis acids.

Lewis acid	$\Delta\tau_{MH}$	ν (M–H), cm^{-1}	$\Delta\nu$ (M–H), cm^{-1}	References
		Complexes with Cp_2MoH_2		
BF_3	—	1855	+5	[28]
$AlHCl_2$ *	—	1855	+5	[30]
$AlCl_3$	—	1850	0	[24]
$AlHBr_2$ **	—	1850	0	[24]
$AlEt_3$	+0.27	—	—	[27]
$ZnCl_2$	+1.3 ***	1810, 1780	—55	[30]
ZnI_2	—	1795, 1740	—80	[30]
ZnI_2·THF	—	1830, 1780	—45	[30]
$FeCl_2$	—	1760, 1720	—110	[29, 135]
$FeBr_2$	—	1750, 1680	—135	[29, 135]
FeI_2	—	1703, 1653	—170	[29, 135]
FeI_2·THF	—	1820, 1740	—70	[29, 135]
CoI_2	—	1708	—142	[29, 135]
$Rh(PPh_3)_3$	+5.52	—	—	[136]
CuCl	—	1690, 1650	—180	[29, 135]
CuI	—	1660, 1650	—195	[29, 135]
		Complexes with Cp_2WH_2		
BF_3	—	1937	+17	[28]
$AlHCl_2$ *	—	1952	+32	[24]
$AlCl_3$	—	1945	+25	[24]
$AlHMe_2$	+0.19	—	—	[131]
$AlMe_3$	+1.00	1905	—15	[131]
$ZnCl_2$	+0.7 ***	1895, 1855	—45	[30]
ZnI_2	+0.2 ***	1885, 1845	—55	[30]
ZnI_2·THF	—	1920, 1870	—25	[30]
$FeCl_2$	—	1860, 1807	—85	[29, 135]
FeI_2	—	1830	—90	[29, 135]
FeI_2·THF	—	1900, 1825	—55	[29, 135]
$CoCl_2$	—	1868	—52	[29, 135]
CuCl	—	1775, 1723	—170	[29, 135]
$Rh(PPh_3)$	+5.83	—	—	[136]

*ν(Al–H) = 1910 cm^{-1}. **ν(Al–H) = 1890 cm^{-1}. ***Solution in DMF.

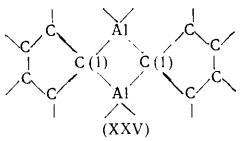
The structure of both molybdenum complexes was established by X-ray diffraction (Fig.3).[139,140] Although it was not possible to establish the positions of the hydrogen atoms, the larger Mo–Al distance (2.95–3.00 Å) compared with the Mo–Al distance in the "non-hydride" component of the molecule (2.65 Å) and the presence of an absorption band at 1825 cm^{-1} in the infrared spectrum enabled the authors[137,139,140] to postulate that the hydrogen atoms are located between the Mo and Al(3) atoms [formula (XXIIIa)], which are thus linked by hydrogen bridges. However, ν(M–H) is closer to ν(Mo–H) in Cp_2MoH_2 (1853 cm^{-1}) than to ν(Al–H) (1750

cm^{-1}) [116] and is not characteristic of bridging hydrogen atoms. One can therefore assume that terminal hydrogen atoms linked to molybdenum are present in the $C_{25}H_{35}Al_3Mo_2$ structure. The Mo–Mo distance (4.75 Å) is entirely sufficient to accommodate two hydrogen atoms [formula (XXIV)].



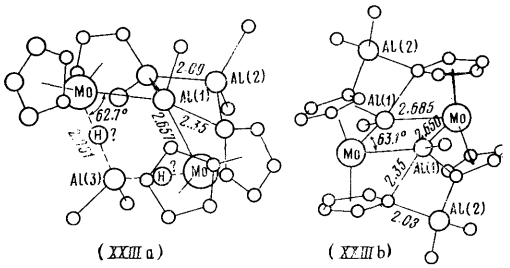
(XXIV)

It is of interest that the cyclopentadienyl group C_5H_4 is tridentate, as in aluminium titanium hydrides[17,54], forming, apart from the σ-bond with the transition metal atom, also a four-centre σ-bond with two aluminium atoms [formula (XXV)].



(XXV)

All the aluminium atoms and the C(1) carbon atom are then in one plane[139,140]. An analogous type of bond has been observed in the ferrocenylalanes $Me_2Al(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4Fe\text{-}\eta^5\text{-}C_5H_5)AlMe_2$.[141,142]

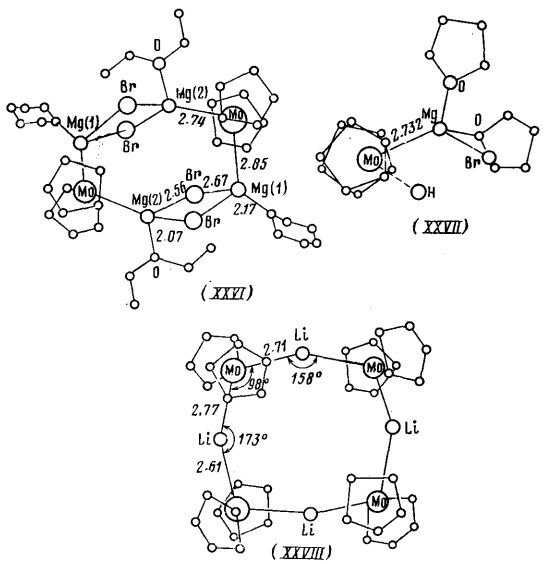


(XXIII a) (XXIII b)

Figure 3. The structures of the $C_{25}H_{35}Al_3Mo_2$ (XIIIa) and $C_{26}H_{34}Al_4Mo_2$ (XXIIIb) molecules according to X-ray diffraction data[139,140].

When solutions of $Cp_2MoH_2(Cp_2WH_2)$ interact with an excess of a Grignard reagent RMgX in ether, yellow crystals of $[Cp_2Mo(H)Mg(R)\text{–}\mu\text{-}X_2Mg(OEt_2)]_2$ (XXVI) are deposited[138,143,144]. An X-ray diffraction study has been made of the compound with R = cyclohexyl [144] (Fig.4). The positions of the hydride hydrogen atoms have not been established. The infrared spectrum of the compound contains absorption bands at 1740 and 1720 cm^{-1}, which are displaced to 1260 cm^{-1} on deuteration. It has been suggested that the terminal hydrogen atoms are in the Mg_aMoMg_b plane, i.e. as in the complex with trimethylaluminium[73], and do not form a bond with the Mg atom. All three orbitals of Cp_2Mo are used up in the formation of bonds with hydrogen and two magnesium atoms (the length of the covalent Mo–Mg bond is shorter by ~0.1 Å than the coordinate bond)[144].

A Lewis base stronger than Cp_2MoH_2, for example, THF, displaces it from the complex with RMgX. Thus, when the BHC $[Cp_2Mo(H)Hg(Br)\mu\text{-}Br_2Mg(OEt_2)]_2$ was dissolved in THF, a red solution was formed, from which the monomeric BCH $Cp_2Mo(H)MgBr.2C_4H_8O$ (XXVII) was isolated[23,145,146]. X-Ray diffraction study of this compound demonstrated the presence of a direct Mo–Mg bond (Fig.4). The magnesium atom is solvated by two THF molecules and has C.N. = 4. The hydride hydrogen atoms are not localised, but ν(Mo–H) = 1850 cm^{-1} is very close to ν(Mo–H) for Cp_2MoH_2 (1853 cm^{-1}).[23] It has been suggested[108] that analogous compounds are formed on interaction of Cp_2MH_2 with RMgX in proportions of 1 : 1. According to Aripovskii et al.[143], the interaction of Cp_2MH_2 with Grignard reagents can proceed via three pathways (Scheme 3), depending on the conditions, with formation of solvated or non-solvated substances, but never leads to the formation of the adducts $Cp_2MH_2.RMgX$. The reaction of Cp_2MH_2 with BeX_2 in ether is significantly reversible.

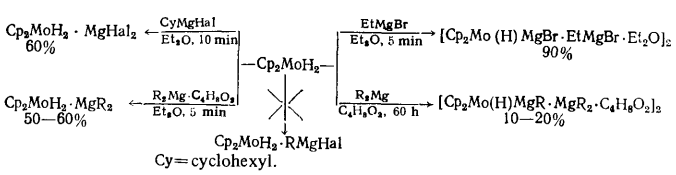


(XXVI) (XXVII) (XXVIII)

Figure 4. The molecular structures of $[Cp_2Mo(H)Mg(C_6H_{11}).(\mu\text{-}Br)_2Mg(OEt_2)]_2$ (XXVI),[144] $Cp_2Mo(H)MgBr.2C_4H_8O$ (XXVII),[23,145] and $[Cp_2Mo(H)Li]_4$ (XXVIII).[148]

Treatment of $Cp_2Mo(W)H_2$ with butyl-lithium in toluene at 50 °C gives rise to the yellow-orange crystals of $[Cp_2Mo(W).(H)Li]_4$ (XXVIII).[147]

Scheme 3



Cy = cyclohexyl.

It was established by X-ray diffraction that complex (XXVIII) is tetrameric and that association takes place via lithium bridges (Fig.4). The Li–Mo–Li angle (97–98°) is unduly large and suggests that hydrogen atoms are present in its bisector plane[148].

The fulvalene complex $[CpMo(H)]_2(\mu\text{-}C_{10}H_8)$ reacts analogously with LiBu, forming the lithium derivative $[CpMo(Li)]_2(\mu\text{-}C_{10}H_8)$, whose properties are similar to those of $[Cp_2Mo.(H)Li]_4$.[149] Like the magnesium derivatives, the compounds

$[(Cp_2Mo(W)(H)Li]_4$ are powerful nucleophiles whose properties are similar to those of organolithium compounds[147]. When they interact with $R_3M'Hal$ (M' = Ge or Sn; R = Me or Et), the BHC $Cp_2Mo(W)(H)M'R_3$, with a direct M–M' bond, are formed[150].

The compound Cp_2MH_2 react with ZnR_2 (R = Et or Bu) to form the polymeric complexes $[(Cp_2M)_2Zn]_n$ without M–H bonds[140]. Like all the BHC of molybdenum and tungsten with direct M–M' bonds, they regenerate the initial dihydride on hydrolysis[138,147,149].

A characteristic feature of the structures of the compounds formed by Cp_2MH_2 with compounds of non-transition Group IIIA and in certain cases Group IIA metals is the formation of a direct M–M' bond and the absence of hydrogen bridge bonds. The situation changes significantly on passing to Lewis acids formed by heavy transition metals.

Weakly soluble or insoluble adducts of Cp_2MH_2 with Zn, Cu, Ag, Co, Fe, Mo, and Rh compounds have been obtained in DMF, THF, diethyl ether, and benzene[29,30,134–136]. The reaction with strong bases results as a rule in the formation of the solvated complexes $Cp_2MH_2.M'Hal_{2-n}.L$ (n = 0 or 1); non-solvated substances crystallise from diethyl ether and benzene.

Table 3 shows that the formation of complexes by Cp_2MH_2 with the transition metal and zinc compounds investigated leads to a significant bathochromic shift of the ν(M–H) band (50–250 cm^{-1} and in the compounds with AgCl and $MoOCl_3$ not less than 350 cm^{-1}, since these bands are then masked by the bands of the solvents and the Cp rings) and its splitting into the ν_s and ν_{as} components[29,135], while τM–H is displaced upfield [$\Delta\tau_{M-H}$ = +5.5–+5.8 p.p.m. for $Rh(RPh)_3$].[136] This is undoubtedly characteristic of the formation of hydrogen bridge bonds analogous to the M–H–B bonds in transition metal hydroborates[11].

Table 4. Structural characteristics of the adducts of Cp_2MH_2 with transition metal and zinc compounds.

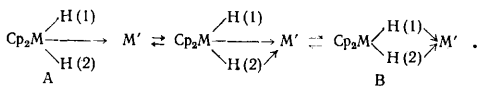
Compound	Interatomic distance r, Å						H(1)MH(2) angle, °	References
	$r_{M-H(1)}$	$r_{M-H(2)}$	$r_{M'-H(1)}$	$r_{M'-H(2)}$	$r_{M-M'}$	$r_{M'-X}$		
$Cp_2MoH_2 \cdot FeI_2 \cdot THF$	1.58	1.86	2.15	1.79	2.854	2.65	85.5	[151]
$[Cp_2MoH_2 \cdot CuI]_2$	1.32	1.97	2.02	1.57	2.73	2. 60, 2. 63	79	[101]
$[(Cp_2MoH_2)_2Cu]CuCl_2$	1.7	2.0	2.0	1.7	2.65	2.17	85	[152]
$Cp_2MoH_2 \cdot ZnBr_2 \cdot DMF$	1.40	1.73	1.78	1.59	2.793	2. 41; 2. 43	63.8	[134]
$Cp_2WH_2 \cdot Rh(PPh_3)_2$	—	—	—	—	—	2.16	—	[136]

X-Ray diffraction study of the compounds $Cp_2WH_2Rh(PPh)_3$,[136] $Cp_2MoH_2ZnBr_2.DMF$,[134] $[Cp_2MoH_2CuI]_2$,[101] $Cp_2MoH_2FeI_2.THF$,[151] and $[(Cp_2MoH_2)Cu].CuCl_2$ [152] confirmed the conclusions reached in other investigations[29,30,135] concerning the presence in these compounds of the bridge bonds



M' and, in contrast to the "classical" symmetrical bridge[11], in the last four compounds asymmetric hydrogen bridges were discovered (Table 4 and Fig. 5; the coordinates of the hydrogen atom were not determined by Alcock et al.[136], while Grotty et al.[134] determined them with a large error).

The question of the degree of involvement of the d^2 electrons of the Mo and W atoms in the formation of a bond with the M' atoms remains open. On the basis of the theoretical model of Alcock and Green[85,86], some investigators[101,151,152] suggest that not only the interatomic distance but also the H(1)MH(2) angle is a measure of the degree of direct M–M' bonding. In compounds with an angle H(1)MH(2) > 90° (A), a direct intermetallic bond is formed preferentially (adducts with halogenoalanes). When the H(1)MH(2) angle is 80–90° (B) and for the corresponding interatomic distance, both a donor–acceptor bond and a hydrogen bridge bond can be formed, whereas in the case of an H(1)MH(2) angle less than 80° (C) the hydrogen bridge bond makes the main contribution to the bonding of the components and the complexes formed are of the chelate type (Cp_2MH_2 is a bidentate ligand) in which the d^2 electrons of the M atom occupy a non-bonding orbital. There is no doubt that the extreme cases are unlikely. Most probably both types of bond obtain to some extent in the compounds considered:



A B

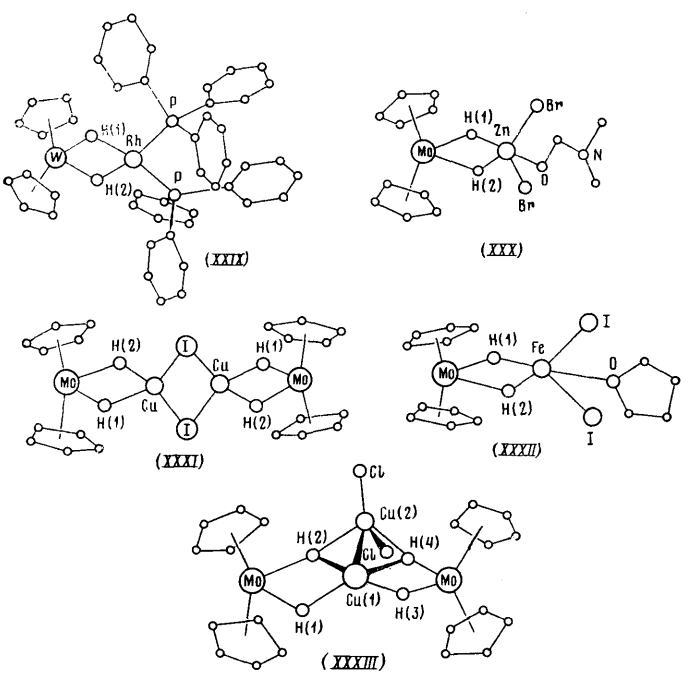


Figure 5. The molecular structures of $Cp_2MoH_2Rh(PPh_3)_2$ (XXIX),[136] $Cp_2MoH_2ZnBr_2.DMF$ (XXX),[134] $[Cp_2MoH_2CuI]_2$ (XXXI),[101] $Cp_2MoH_2FeI_2.C_4H_8O$ (XXXII),[151] and $[(Cp_2MoH_2)_2.Cu]CuCl_2$ (XXXIII).[152]

VI. MONO- AND TRIS-CYCLOPENTADIENYL BIMETALLIC HYDRIDE COMPLEXES

The introduction of even one π-C_5H_5 group into the coordination sphere of a transition metal atom increases significantly the stability of hydride compounds. The monocyclopentadienyl BHC have apparently a structure similar to that

of the biscyclopentadienyl complexes, although their stability is lower.

When $CpTiCl_3$ is reduced with metallic magnesium in the presence of MgI_2, the EPR spectrum exhibits a triplet with the intensity ratios 1 : 2 : 1, analogous to the signal of the compound $Cp_2Ti\begin{smallmatrix}H\\ \diagup\ \diagdown\\ H\end{smallmatrix}MgI$ [60] and apparently corresponding to the BHC $Cp(Cl)TiH_2^-MgI^+$. As in the case of the biscyclopentadienyl complex, the source of the hydride hydrogen is the Cp rings, since the EPR signal does not appear when $CpTiCl_3$ is replaced by $(C_5Me_5)TiCl_3$.[60]

The possibility of obtaining monocyclopentadienyltitanium BHC stable under ordinary conditions has been confirmed by the results of the calorimetric titration of $CpTiCl_3$ with lithium tetrahydroaluminate in diethyl ether: the reaction proceeds via the same stages as that involving Cp_2TiCl_2 and the enthalpy changes are similar[37]. It is of interest that the stage involving the substitution of the last chlorine atom by a hydrogen atom is not accompanied by an enthalpy change in this instance, as in the case of $(Cp_2V)_2ClAlH_2$.[122] The final reaction product is the complex $CpTi(AlH_4)_2.AlH_3$, which is extremely unstable and decomposes after 10–20 min with the complete evolution of hydrogen.

In the study of the polymerisation of ethylene in the presence of the Cp_4Zr–$AlEt_3$ system, the BHC (XXXV), stabilised by three C_5H_5 groups, was isolated[153]:

$$Cp_4Zr \xrightarrow[-C_2H_4]{AlEt_3} Cp_3ZrEt \xrightarrow[-C_2H_6]{AlEt_3} Cp_3ZrCH_2AlEt_2 \xrightarrow[-C_2H_4]{AlEt_3} Cp_3ZrCH_2CH\begin{smallmatrix}AlEt_2\\ \diagdown\\ AlEt_2\end{smallmatrix}$$

$$Cp_3ZrH\cdot Al(Et)CH{=}CH_2 \rightleftarrows (XXXIV) \rightleftarrows Cp_3ZrH + {}^1/_2(AlEt_3)_2. \qquad (51)$$

The formula $Cp_3Zr{-}H{-}AlEt_3$ (XXXIV) was proposed on the basis of the chemical properties and preliminary X-ray diffraction data (Zr–Al = 3.66 Å). It may be that similar BHC are also formed in the Cp_2ZrX_2–$AlEt_3$ system[154,155].

Triscyclopentadienyluranium(IV) forms bimetallic complexes in solution with alkyl groups and halogen bridges of the type $Cp_3U\begin{smallmatrix}R\\ \diagdown\\ Al\\ \diagup\\ U\\ \diagdown\\ R\end{smallmatrix}R$,[156] but the BHC could not be isolated in a pure state owing to the rapid reduction of uranium(IV) to uranium(III).[157]

VII. BIMETALLIC TRANSITION METAL HYDRIDE COMPLEXES STABILISED BY OTHER ELECTRON-DONATING LIGANDS

Apart from the fairly numerous and comparatively thoroughly investigated biscyclopentadienyl BHC, there are extremely few data on BHC stabilised by other electron-donating ligands such as alkyl groups, olefins, and phosphorus- and oxygen-containing Lewis bases. The conclusion concerning the structure of the majority of the complexes formed under these conditions is exceptionally tentative and we shall therefore consider only briefly the available literature data on this question.

Thus the stabilisation of the transition metal hydride complexes has been noted in complex multicomponent catalytic systems of the Ziegler–Natta type, where the stabilisers are solvents, the substrate, and non-transition metal compounds.

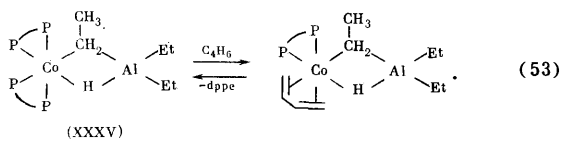
Although the majority of the transition metal hydrides obtained at the present time contain organophosphorus ligands, the BHC stabilised by phosphines or phosphites are almost unknown. The only reliably characterised BHC of this group is the compound $\{Ta[H_2Al(OC_2H_4OMe)_2](dmpe)_2\}$, where dmpe = bisdimethylphosphinoethane $Me_2PCH_2CH_2PMe_2$ obtained by reaction (52).[158] The complex is a dimer linked by Al–O–Al bridges:

$$TaCl_2(dmpe)_2 + NaAlH_2(OC_2H_4OMe)_2 \xrightarrow{Et_2O} [Ta\{H_2Al(OC_2H_4OMe)_2\}(dmpe)_2]_2 + NaCl + H_2 + AlH(OC_2H_4OMe)_2, \qquad (52)$$

The P_4TaAl atomic group is a distorted square pyramid (as a consequence of the formation of the TaH_2Al bridge, the angle between the normal to the P_4 plane and the Ta–H bond is 16°). The H atoms are not localised but the infrared spectrum shows two equally intense bands at 1605 and 1640 cm^{-1}, which the authors attribute to the presence of two bridging hydrogen atoms.

A series of BHC have been obtained in Ziegler–Natta systems modified by phosphines. BHC having the composition $[Fe(dppe)_2]^+[AlH_2R_2]^-$ are formed in the $Fe(acac)_3$–$AlEt_3$–dppe system, where dppe = bisdiphenylphosphinoethane $Ph_2PCH_2CH_2PPh_2$ and acac = acetylacetone[15]. In contrast to the complex $[Fe(dppe)_2]^+[AlCl_2R_2]^-$, which has a similar composition, this compound does not decompose on treatment with diethyl ether[15], which indicates a more complex Fe–AlH_2R_2 interaction than was suggested on the basis of the ionic mechanism.

The codimerisation of ethylene and butadiene in the presence of $CoCl_2$–$AlEt_3$–dppe is believed to proceed in the presence of complex (XXXV), which readily splits off phosphines[159]:



(XXXV) (53)

The BHC having the general formula $[HNiL_n]^+AlX_4^-$ are formed in the NiX_2–$AlR_3(AlX_3')PR_3'$ systems, which are active in the dimerisation of olefins[22,160–162]. The non-transition metal compound plays the role of the Lewis acid and can be replaced by, for example, $TiCl_4$.[22]

The proposed structure of the BHC has been confirmed by specific synthesis from $HNiCl(PPr_3)_2$ and $AlCl_3$ [in this process $\nu(Ni{-}H_{ter})$ = 1937 cm^{-1} shifts slightly towards longer wavelengths[160]] and also from $Ni(dppe)_2$ and $HAlCl_4$.[163]. It is noteworthy that $\nu(Ni{-}H)$ = 1949 cm^{-1} and τ_{Ni-H} = 23 for the complex with dppe hardly change when the $AlCl_4^-$ anion is replaced by BF_4^-.[163] The isolation of the stable (up to 125 °C) BHC having the composition $Cp_2FeH^+AlCl_4^-$ has also been reported[164]. Only the BHC containing nickel(II) are active in the $NiCl_2$ + $AlEt_3$ + PR_3 system.[161,162] The formation of BHC has also been postulated in the $CoCl_2$–RMgCl–dppe system[165].

In the fixation of nitrogen in the presence of the $TiCl_3.(VCl_3)$–Mg–THF system, the nitride complex $[MNMg_2Cl_2.THF]$ is formed and reacts with H_2 in the presence of Mg to form the BHC $[TiH_2NMg_3Cl_{1.5}.(THF)_x]$.[166,167] The reduction of VCl_3 with magnesium in THF in an argon atmosphere gives rise to a BHC having a similar composition, namely $[VHMg_2.Cl_{1.5}(THF)_x]$, while reduction in an H_2 atmosphere results in the formation of $[VH_2MgCl(THF)_2](THF)_2$.[167,168] The $\nu(M{-}H)$ absorption band has not been observed in the infrared spectra of the two complexes[166]. Analogous BHC are apparently formed also in the MX_n–Mg systems for compounds of other transition metals[168]. These compounds catalyse the hydrogenation of olefins. It is of interest that the introduction of aluminium chloride into the VCl_3–Mg system up to the ratio Al : V = 1 : 1 increases the rate of hydrogenation[167], which is believed to be due to the substitution of Mg by aluminium in the BHC.

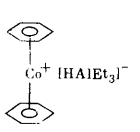
BHC containing a Group VIII metal and magnesium are formed in Ziegler–Natta systems with Grignard reagents. Thus the $FeCl_3$–PhMgBr system absorbs hydrogen, which is attributed to the formation of BHC of the second type[169]. Subsequently the complex $FeH_2MgX_4(THF)_8$ was isolated in a pure state in the form of a yellow crystalline substance[170]:

$$FeCl_3 + 7PhMgBr + 6H_2 \xrightarrow{THF} \tfrac{1}{2}\,Ph{-}Ph + 3MgX_2 + 6C_6H_6 + FeH_6Mg_4X_4(THF)_8. \quad (54)$$

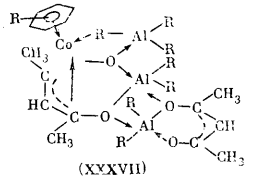
The existence of the catalytically active BHC with Co–H–Al bridge bonds and stabilised by THF has been postulated in the $CoCl_2$–$NaAlH_2(OMe)_2$ system prepared in an H_2 atmosphere[171].

A complex dihydride, active in the hydrogenation of olefins, is formed in the cobalt(nickel, iron) stearate–RMgX systems in diethyl ether; it is believed to be stabilised by the products of the interaction of the stearate and a Grignard reagent[172,173].

The interaction in cobalt chelates–AlR_3(LiR, RMgX) systems gives rise to a series of cobalt(I) and zerovalent cobalt complexes stabilised by aromatic hydrocarbons and transition metal compounds[174,175]. The formation of the BHC (XXXVI) [174] and of the alkyl complex (XXXVII),[175] which in the course of hydrogenation apparently gives rise to compounds (XL), has been postulated:



(XXXVI)



(XXXVII)

An unusual BHC, stabilised by an olefin and THF and having the composition $(COD)_{1.5}NiLi_2H_2(THF)_x$ (COD = cyclo-octadiene) has been obtained in accordance with Eqn. (55). The complex reacts with CO, liberating cyclo-octadiene but not H_2.[176] As regards chemical properties, it behaves as a lithium hydride transferring agent, its reaction with $AlEt_2$, for example, yielding $Li[AlHEt_3]$, but, in contrast to pure LiH, it reacts with olefins, forming lithium alkyls:

$$(COD)_2Ni + 2Li \xrightarrow{THF,\ -30^\circ} (COD)_2NiLi_2(THF) \xrightarrow{+H_2,\ -60^\circ} (COD)_{1.5}NiH_2Li_2(THF)_x. \quad (55)$$

It is of interest to consider the possible ways of seeking new BHC, which evidently involves their stabilisation by effective ligands other than the C_5H_5 groups. As stated above (Section III, Subsection 5), the stability of the transition metal tetrahydroaluminates $M(AlH_4)_n$ varies in parallel with the stability of the corresponding tetrahydroborates. The same behaviour has been observed also for other BHC: stable tetrahydroaluminates correspond to the stable monocyclopentadienyltitanium tetrahydroborate[177] and biscyclopentadienyltitanium, biscyclopentadienylzirconium, biscyclopentadienylvanadium, and biscyclopentadienylniobium tetrahydroborates[11]. Consequently stable transition metal tetrahydroborate complexes can be regarded as models in relation to the tetrahydroaluminate complexes. However, it is noteworthy that, since the coordinating capacity of the aluminium atom is greater than that of the boron atom and the AlH_4^- group is a stronger reductant than BH_4^-, it is to be expected that the structure of the tetrahydroaluminate BHC differs significantly in most cases from that of the tetrahydroborate BHC (see, for example, Erofeev et al.[122] and Marks and Kennelly[178]).

Transition metal tetrahydroborates stabilised by phosphines and also arsines have been described for cobalt, nickel, ruthenium, rhodium, iridium, palladium, copper, and silver[11] as well as molybdenum[179]. Carbonyl compounds are also known: the stable salt $[(Ph_3P)_4N]^+[Mo(CO)_4BH_4]^-$ and the unstable complex $Mn(CO)_5BH_4$.[11] The stable trisdialkylaminotitanium(IV) [180] and trisdialkylaminothorium(IV) [181] tetrahydroborates and uranium(III) tetrahydroborate, stabilised by crown-ether[182], are noteworthy.

Bearing in mind the synthesis in recent years of a large number of stable transition metal alkyls with substituents not containing β-hydrogen atoms, one may expect the synthesis of BHC containing such alkyl groups. Thus a series of zinc tetrahydroaluminate complexes having the general formula $MZn_nMe_{2n}AlH_4$, where M = Li, Na or K and n = 1 or 2, which are stable in solution in THF, have been obtained by Ashby and Watkins[183–185].

Another possible method of synthesis of stable BHC involves the interaction of non-transition metal compounds with molecular transition metal hydrides. Among these, we may note the familiar pentahydrides $MH_5(dmpe)_2$ of niobium[186] and tantalum[187], whose chemical properties resemble closely those of Cp_2MH_3: they catalyse the H–D exchange between D_2, on the one hand, and C_6H_6 and C_2H_4, on the other, and form the complexes $NHL_2(dmpe)_2$ with CO and C_2H_4. Analogous complexes having the composition $MH_3(dmpe)$ have also obtained for titanium and zirconium[188]. The synthesis of $CpNb(PPh_3)_2(CO)H_2$, isoelectronic with Cp_2MoH_2,[189] and of $CpMo(dppe)H_3$, isoelectronic with $CpNbH_3$,[190] has been reported. The chemistry of BHC involving the study of the complex-formation reactions of Cp_2MH_n and the isoelectronic compounds Cp_2NbH, $(PR_3)_4MH_4$,[191] etc. with transition metal compounds will apparently be fairly fruitful.

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Synthetic Methods for Cyclohexa-1,3-dienes

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The review gives a systematic account of the methods of synthesis of cyclohexa-1,3-diene, its homologues, and derivatives with functional groups. The purity of the preparations obtained by each method is considered on the basis of modern data. The bibliography includes 221 references

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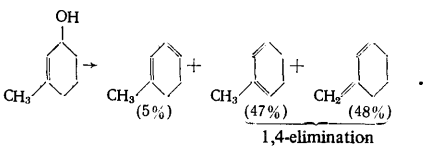
I. INTRODUCTION

Substituted cyclohexa-1,3-dienes are important intermediates in the synthesis of many physiologically active compounds, including terpenes, carotenoids, and steroids. Cyclohexa-1,3-diene (I) itself has been used as the starting material in one of the schemes for the stereoselective synthesis of 11-deoxyprostaglandines[1]. It is a promising monomer for the manufacture of aromatisable polymers. Both the diene (I) itself and the vast majority of its derivatives (with the possible exception of α-terpinene and α-phellandrene) are obtained solely by synthesis. Despite the importance of this class of compounds, there is no review literature on the methods of their synthesis. The aim of the present review is to fill this gap†. The methods of synthesis of the diene (I), its homologues, and derivatives with functional groups are relatively varied. The principal methods can be divided into five groups in the majority of which the starting material contains the cyclohexane ring. The synthesis of the diene (I) and in the first place its homologues and derivatives involves certain experimental difficulties. Many of the synthetic methods result in the formation of side products, including isomeric dienes. The high reactivity of cyclohexadienes, particularly their tendency to dimerise, polymerise, aromatise, and oxidise, may also be the cause of the reduced yield of the desired products and the appearance of impurities. The principal causes of the possible inhomogeneity of cyclohexa-1,3-dienes are considered below.

II. THE AMBIGUITY OF THE REACTIONS AND THE PRINCIPAL SIDE PROCESSES

1. The Mode of Elimination and the Admixture of 3-Methylenecyclohexenes

The formation of the second double bond in the cyclohexadiene ring is usually achieved with the aid of elimination reactions (the elimination of hydrogen halides, water, alcohol, etc.) which can occur via different pathways even under mild conditions: via 1,2- and 1,4-elimination mechanisms[2]. The 1,4-elimination product can predominate, which is confirmed by the data in Tables 1 and 2 (see below). The dehydration of substituted cyclohex-2-en-1-ols leads as a rule to mixtures of two dienes with endocyclic double bonds and, in the presence of an alkyl group in the 1- and 3-positions, is accompanied by the formation of an admixture of 3-methylenecyclohex-1-enes. The amount of the latter in the mixtures can be very considerable (in excess of 40%), for example[3]:



The elimination of two water molecules (from cyclohexanediols) or two hydrogen halide molecules (from dibromocyclohexanes) evidently proceeds with intermediate formation of the allyl system and hence should also obey the rule mentioned above.

2. Admixture of Cyclohexa-1,4-dienes

When two water molecules are split off from cyclohexane-1,3-diols or cyclohexane-1,4-diols, cyclohexa-1,4-diene is formed as a side product in an amount of 20% and above (see below). It is reasonable to suppose that isomers with isolated double bonds can also be present in the dehydrobromination products of 1,3- and 1,4-dibromocyclohexanes (particularly the latter). Cyclohexa-1,4-dienes can also be formed as the products of the isomerisation of the corresponding 1,3-dienes in an alkaline medium.

3. Isomerisation

The isomerisation of cyclohexa-1,3-dienes can occur as a result of a 1,5-shift of hydrogen (above 250 °C), a 1,5-shift of substituents (400–500 °C), and a change in the nature of the substituent (500–600 °C).[4] The processes lead to the formation of a mixture of isomers with different positions of the double bonds and under the conditions of pyrolysis complex mixtures of skeletal isomers are produced.

In the presence of strong bases (for example, solutions of alkali metal alkoxides in the corresponding alcohols or dimethyl sulphoxide, (DMSO), cyclohexa-1,3-diene itself is partly converted into the 1,4-isomer (see, for example, Refs.5–8). The amount of the latter in the mixtures formed depends greatly on the nature of the base, the solvent, and other isomerisation conditions, varying in the range 0–34%;

† The literature up to 1945 is excluded from consideration.

cyclohexa-1,4-dienes is capable of isomerising quantitatively to the corresponding conjugated dienes under the influence of the same bases in ammonia, amines, and other solvents.

4. Aromatisation

A specific feature of the cyclohexa-1,3-diene derivatives is the ease with which they are aromatised. The conversion of dienes of the above series into benzene derivatives takes place as a result of two related reactions—dehydrogenation and disproportionation—with the simultaneous formation of cyclohexenes.

Cyclohexa-1,3-dienes can be dehydrogenated on heating in the liquid or gaseous phase with substances capable of absorbing hydrogen or with oxidants; the most thoroughly investigated hydrogen absorbing agents are palladium on charcoal[9–15] and elemental sulphur[16,17]. In the vapour phase above 400 °C, the dehydrogenation of cyclohexa-1,3-diene takes place in the absence of catalysts with evolution of molecular hydrogen[2,18–20]. The degree of conversion is then considerable (approximately 50%) only at 500 °C. Thermal aromatisation of the 5,5-disubstituted cyclohexa-1,3-dienes takes place via dealkylation (with evolution of a gaseous alkane) at 550 °C [21,22] and above.

It is generally known that the disproportionation of cyclohexa-1,3-dienes can occur as a heterogeneous process—as a result of contact with catalysts: palladium, platinum, nickel, and iron at 50–100 °C or alumina at 250–400 °C.[23] Homogeneous disproportionation takes place when dienes interact with strong bases under exceptionally mild conditions. Thus, when cyclohexadienes come into contact with a solution of potassium t-butoxide in DMSO (55 °C, 24 h) [7] or t-butyl alcohol (60°, 3h),[24] the dienes are quantitatively converted into a mixture of equal amounts of aromatic and mono-olefinic compounds. Sodium amide in liquid ammonia in the presence of a proton donor (for example, ammonium chloride) exhibits a powerful disproportionating activity[8]. Thermal disproportionation of the diene (I) takes place when it is heated for a long time at 150–200 °C in the absence of a solvent or catalyst during dimerisation[25] or polymerisation[26–28], the overall yield of benzene or cyclohexene reaching 20%.

5. Dimerisation and Polymerisation

Dimerisation via the diene condensation mechanism (see, for example, Refs. 25, and 29–31) and thermal polymerisation (see, for example, Refs. 27, 28, 32, and 33) take place as parallel reactions on heating cyclohexa-1,3-diene at 170 to 200 °C; the process is completed by the complete disappearance of the monomer in the course of approximately 10 h. The polymerisation of the diene (I) is catalysed by Lewis acids and takes place even at −80 °C in the presence of titanium tetrachloride[34–39], tin tetrachloride[34], or boron trifluoride[38,39]. On treatment with n-butyl-lithium, the polymerisation takes place at 30–60 °C.[36,37,40].

6. Oxidation

Cyclohexa-1,3-diene[41,42] and its derivatives[42] are oxidised by oxygen, particularly readily in the light, to endoperoxides even at room temperature; under the same conditions, not only the oxidation but also the aromatisation of dienes is observed[43].

7. Practical Recommendations

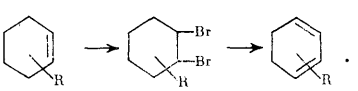
The foregoing shows that, in selecting a scheme for the synthesis of a substituted cyclohexa-1,3-diene, one must take into account many factors which can be reflected in the purity of the preparation. In the synthesis of cyclohexa-1,3-dienes, prolonged heating at 170 °C and above is undesirable (dimerisation, polymerisation, and disproportionation) and even brief heating at 250 °C can be damaging (isomerisation), while temperatures of 400 °C and above (dehydrogenation) must be completely ruled out. In synthetic methods the use of Lewis acids is inadmissable (polymerisation) and contact with strong bases (isomerisation and disproportionation), alumina, particularly at an elevated temperature (disproportionation), and atmospheric oxygen (oxidation and dehydrogenation) can have undesirable consequences.

The number of specimens of substituted cyclohexa-1,3-dienes described in the literature is very large but the purity and isomeric composition of the preparations have been checked only in studies during the last two decades. Analysis of the early literature data shows that the vast majority of the cyclohexadiene specimens could not have been homogeneous and hence the employment of these data in synthetic practice requires a preliminary aasessment of their reliability.

III. SYNTHESIS OF CYCLOHEXA-1,3-DIENES

1. Synthesis from Cyclohexenes

(a) *Bromination–dehydrobromination.* The most frequently employed scheme for the synthesis of cyclohexadienes from cyclohexenes involves bromination–dehydrobromination:



The bromination of cyclohexene (II) or its homologues is carried out at −5–0 °C in chloroform[32], carbon tetrachloride[44], or glacial acetic acid[45]; in all cases the reaction leads to the corresponding 1,2-dibromo-derivatives in yields of 80–85%. In the method ensuring the maximum yield of the dibromo-derivative (95%),[46] carbon tetrachloride with added absolute ethanol was used as the solvent.

Quinoline at the boiling point was widely used in early studies as the dehydrobromating reagent; the dienes were isolated from the reaction mixture by distillation (yield 45 to 65%). It has been shown by Raman[47] and ultraviolet[48] spectroscopy and also by gas-liquid chromatography (GLC) [35] that the composition of the preparation obtained by this method incorporates 40–50% of the diene (I), 40–50% of cyclohexene (II), and approximately 20% of benzene. It is extremely difficult to separate these compounds (b.p. 80.5°, 83°, and 80 °C respectively) by fractional distillation. The isolation of the pure diene (I) via its complex with silver nitrate[49] is suitable only for small batches of the diene.

The above method was used in early studies to obtain cyclohexadienes from 1-methyl-, 5-methyl-, 1,3-dimethyl-, and 1,4-dimethyl-cyclohexenes. The compositions of the dienes enumerated above were not monitored but it was shown by ultraviolet spectroscopy[50] that "5-methyl-cyclohexa-1,3-diene" obtained by this method contains 58% of toluene. According to Domnin's data[51], the dehydrobromination of 1,2-dibromo-1-chlorocyclohexane by quinoline led to chlorocyclohexadiene considerably contaminated by chlorocyclohexene and chlorobenzene. From the above, all the preparations of substituted cyclohexadienes obtained by the method described

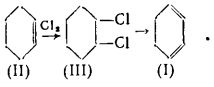
should contain not more than 50% of the main substance. Furthermore, as a result of the different pathways followed in the elimination of the second molecule of hydrogen bromide, there is a possibility of the formation of mixtures of isomers.

It has been suggested that 1,2-dibromocyclohexane be dehydrobrominated[44] by the readily available sodium alkoxide derived from ethylene glycol (at 220–230 °C) with the distillation of the reaction products; the yield of the hydrocarbon fraction is then 60%; according to infrared spectroscopic data, the resulting mixture contains 81% of the diene (I), 4% of the benzene, and 15% of cyclohexene (II). Despite the only slight increase of the yield and purity of the preparation obtained, this method has an advantage over that described above, since the expensive quinoline is replaced by the readily available sodium hydroxide and ethylene glycol. It is known[52] that, when sodium hydroxide is replaced by potassium hydroxide, the yield of the diene (I) increases to 71%, but its purity was not estimated. Presumably the specimen obtained is also not free from benzene and cyclohexene as impurities.

It has been suggested that a solution of sodium isopropoxide in aprotic solvents (for example, in the dimethyl ether of triethylene glycol) be used as the dehydrobrominating agent at 110–115 °C with distillation of the products *in vacuo*[53]. The yield of the diene (I) is then 35–40%. It is known[53] that an increase of the reaction temperature leads to the contamination of the product by benzene and cyclohexene. It has been established[54] that the application of a similar method (involving the use of sodium methoxide), for the synthesis of substituted cyclohexadiene leads to extremely complex mixtures of products.

Thus a change in the nature of the dehydrobrominating agent has still not permitted the synthesis of individual cyclohexadienes by means of the scheme described.

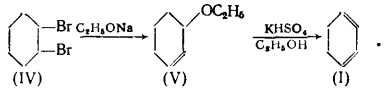
(b) *Chlorination–dehydrochlorination.* A scheme based on the chlorination of cyclohexene with subsequent thermal[55] or catalytic[56] dehydrochlorination of the resulting 1,2-dichlorocyclohexane (II) has been considered as a method of industrial synthesis of the diene (I):



(II) (III) (I)

The addition of chlorine to cyclohexene takes place readily in both liquid and gas phases. According to patent data[57,58], the dehydrochlorination of the dichloro-derivative (III) can be achieved in 89% yield when it is treated with sodium hydroxide in poly(ethylene glycol); the preparation obtained is contaminated by an admixture of 3-chlorocyclohexene[57]; the similarity of the dehydrohalogenation method to that described above suggests that the preparation should contain also benzene and cyclohexene. In order to achieve a continuous process, it has been suggested[56] that the vapour of the dichloro-derivative (III) be passed over alumina and silica gel, deposited on activated charcoal, at 300 °C and a pressure of 100 mmHg. The yield of the diene (I) is 33%, but, according to GLC data, the preparation is contaminated by benzene (10%), methylcyclopentadienes (7%), and methylcyclopentenes (3.5%). A patent has been taken out[55] for the pyrolytic (230–480 °C) dehydrochlorination of the dichloro-derivative (III), which results in a 34% yield of the diene (I) together with 7% of benzene and small amounts of cyclohexene and cyclohexa-1,4-diene. Thus the scheme described requires extensive further elaboration for its practical realisation.

(c) *The Hofmann–Damm method.* The scheme proposed by Hofmann and Damm[32] for the dehydrobromination of 1,2-dibromocyclohexane is extremely widely used:

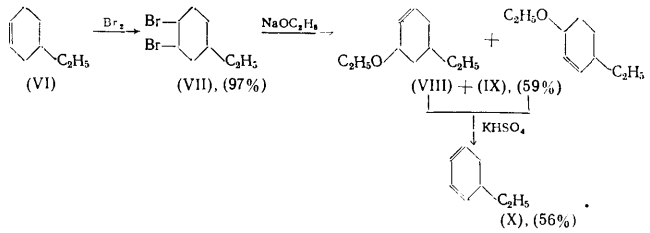


(IV) (V) (I)

Treatment of the dibromo-derivative (IV) with a boiling alcoholic solution of sodium ethoxide leads to a 40–70% yield of 3-ethoxycyclohexene (V) accompanied by the formation of 15–30% of the diene (I). Distillation of the ether (V) from sodium bisulphate makes it possible to split off an alcohol molecule which gives rise to a 60–90% yield of the diene (I). The formation of a mixture of the ether (V) and the diene (I) on treatment of the dibromo-derivative (IV) with sodium ethoxide constitutes a definite disadvantage of the scheme, since this mixture requires separation which inevitably entails losses. The method has been frequently tried and improved[59]. According to Raman spectroscopic data, the preparation obtained is free of admixtures of benzene and cyclohexene.

In one of the versions of this scheme, it has been suggested[60] that sodium ethoxide be replaced by the methoxide (the yield of 3-methoxycyclohexene is 69%) and that methanol be split off by heating (155–160 °C) with orthophosphoric acid in triethylene glycol. The yield of the diene (I) in the last stage is 82%. According to the data of Zupancic and Wucherpfennig[60], the diene (I) formed is chromatographically homogeneous. Sodium isopentoxide has been suggested for the same purpose. A considerable acceleration of the reaction (IV) → (V) (at 130 °C it is almost instantaneous) and the easier elimination of isopentyl alcohol in the second stage have been pointed out as advantages of the above reagent. However, the diene (I) formed under these conditions contains an appreciable amount of cyclohexene as an impurity.

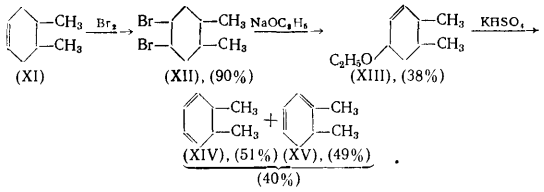
Using the Hofmann–Damm method[32], 1-methyl-,[54] 4-methyl-,[54] 1-ethyl-, 3-ethyl-, and 4-ethyl-,[61] 1-n-propyl-, 1-isopropyl-, 1-n-butyl-, 1,4-dimethyl-, and 4,4-dimethyl-,[21] 4,5-dimethyl,[61] 4-ethyl-4-methyl-,[62] and 1-phenyl- and 1,2-dibromo-cyclohexenes[63] have been converted into substituted cyclohexadienes. The reaction conditions and the yields at different stages reproduce fairly closely those described above for the diene (I) itself. The structure of the preparations of substituted cyclohexadienes obtained was established only in a small number of instances. It is known[61] that the reaction applied to 4-ethylcyclohexene (VI) leads to a fairly homogeneous (approximately 98%) 5-ethylcyclohexa-1,3-diene (X), i.e. there is virtually no migration of the double bonds under the elimination conditions:



(VI) (VII), (97%) (VIII) + (IX), (59%) (X), (56%)

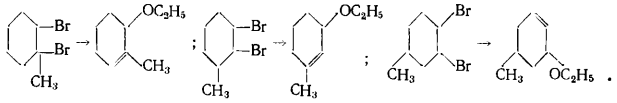
On the other hand[61], under analogous conditions, a mixture of approximately equal amounts of the isomeric dienes (XIV) and (XV), which correspond to different elimination

pathways, is formed from 4,5-dimethylcyclohexene (XI):



(XI) (XII), (90%) (XIII), (38%) (XIV), (51%) (XV), (49%) (40%)

It was later established reliably by GLC and ^1H NMR [64] that the interaction of the methyl-substituted dibromocyclohexenes (XVI)–(XVIII) with sodium ethoxide proceeds via one of the two possible pathways with a selectivity of 95–97%:

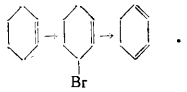


(XVI) (XIX), (51%) (XVII) (XX), (43%) (XVIII) (XXI), (62%)

On the other hand[64], heating of the ethers (XIX)–(XXI) with potassium hydrogen sulphate at 100 °C leads to extremely complex mixtures of hydrocarbons and, apart from the two possible elimination pathways, the mixture composition is complicated also as a result of the isomerisation of the dienes formed. The results of the above study[64] were subsequently reproduced[65].

Thus the above procedure for the synthesis of substituted cyclohexa-1,3-dienes can be of interest only when the starting materials are 4-substituted or 4,4-disubstituted cyclohexenes, since only then do both reaction pathways lead to the same diene. Consequently among the preparations enumerated above, only the 5-methyl-, 5-ethyl-,[61] 5,5-dimethyl-,[21] and 5-ethyl-5-methyl-cyclohexadienes[62] can be relatively homogeneous.

(d) *The Ziegler method.* Cyclohexenes were converted into cyclohexadienes in accordance with the following scheme[66]:



(II) (XXII) (I)

The bromination of cyclohexene with *N*-bromosuccinimide in carbon tetrachloride leads to a 70–85% yield of 3-bromocyclohexene (XXII), whose dehydrobromination with the aid of quinoline at 190 °C results in a 50–70% yield of the diene (I); this method has been frequently employed. According to GLC data[35,40], the preparation obtained is not less than 99% pure and contains only traces of cyclohexene, which appears doubtful on the basis of the comparison with the data presented above. A mixture of 1- and 2-chlorocyclohexa-1,3-dienes was obtained in the same way from 1-chlorocyclohexene[67] and a mixture of 1-methoxycarbonyl-2-methyl- and 1-methoxycarbonyl-6-methyl-cyclohexa-1,3-dienes was obtained from 4-methoxycarbonyl-3-methylcyclohexene[68]. The diene has been synthesised analogously from the nitrile of cyclohexene-1-carboxylic acid[69]. Collidine[49], triethylamine[68], sodium methoxide[69], and potassium t-butoxide[70] have also been used as dehydrobrominating agents, but in all the instances indicated above a decrease of the yield of the desired product was observed.

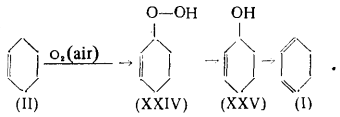
Thus one can assume that the method has no advantages over that discussed above, particularly as regards the synthesis of substituted cyclohexadienes, since the formation of mixtures of isomers from the individual substituted cyclohexene has been demonstrated experimentally in this instance [67,68]. Thus "2-cyanocyclohexa-1,3-diene" [69] and "5-methylcyclohexa-1,3-diene" [71] obtained in this way are most probably mixtures of isomers.

A version of the given scheme is the allyl chlorination of cyclohexene[72] by t-butyl hypochlorite in the presence of benzoyl peroxide (yield 77%) with subsequent dehydrochlorination of 3-chlorocyclohexene by dimethylaniline at 180 °C; the yield of the diene (I) is 80%, but the purity of the preparation has not been established. However, it forms an adduct with maleic anhydride in 93% yield. Bearing in mind that the dehydrochlorination of chlorocyclohexene proceeds much more readily than that of dichlorocyclohexane, this process can be regarded as the most likely industrial scheme for the synthesis of the diene (I) using the high-temperature allyl chlorination of cyclohexene in the first stage (by analogy with the thoroughly investigated propene chlorination process). However, this question has not so far been investigated.

(e) *The allyl oxidation.* The oxidation of cyclohexene with selenium dioxide in acetic anhydride leads to a 50% yield of 1-acetoxycyclohex-2-ene (XXIII). Two distillations of the acetate (XXIII) from potassium hydrogen sulphate at 145 to 155 °C give rise to a 60–70% yield of the diene (I), whose relative homogeneity has been confirmed by the fairly satisfactory agreement of its constants with those of a preparation known to be pure.

In order to convert acetates of type (XXIII) into cyclohexadienes, they were pyrolysed at 420 °C;[73] however, it has been shown for 3-methoxycarbonylcyclohex-1-en-2-yl acetate that the reaction product is a mixture of the possible isomers of methoxycarbonylcyclohexadiene, which is apparently contaminated by the corresponding aromatic compounds, i.e. this method cannot be recommended.

One of the most promising schemes for the industrial application of the syntheses of the diene (I) is[74]



(II) (XXIV) (XXV) (I)

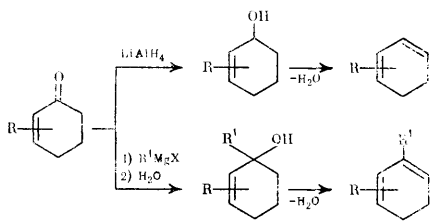
Cyclohexene is usually oxidised by atmospheric oxygen at 150 °C and 25–75 atm. This reaction is known to be autocatalytic[74–77]. The employment of cumenyl hydroperoxide as the catalyst[78] makes it possible to carry out the process under milder conditions (90–100 °C, 6–10 atm). As a rule[75,76,77], the degree of conversion is not high (15–30%) and the unreacted cyclohexene is readily separated by distillation and can be reused. The decomposition of the cyclohexenyl hydroperoxide (XXIV) may entail the formation of cyclohex-2-en-1-one and epoxycyclohexane; their minimal amount (3 to 10%) is obtained when the oxidation product is treated with 1 *N* NaOH at 40 °C [76] or with iron sulphate in alcohol[77]. The conditions for the dehydration of cyclohex-2-en-1-ol, are described below.

Thus the application of the schemes described in this section to the synthesis of cyclohexa-1,3-diene derivatives is undesirable in view of the formation of complex mixtures of isomers. On the other hand, cyclohexene is the most readily available starting material for the synthesis of the diene (I) itself. Among the methods discussed above, the Hofmann–Damm method can yield the purest preparation of cyclohexa-1,3-diene. However, the simplest procedure involving bromination–dehydrobromination with the aid of quinoline or the more readily available alkoxide derived from ethylene glycol

has not lost its importance despite the low purity of the diene obtained, since the impurities do not interfere with many reactions (for example, the diene condensation). The oxidation of cyclohexene and the dehydration of the resulting enol (XXV) are apparently beyond competition at the present time as regards their application on an industrial scale.

2. Synthesis from Cyclohex-2-en-1-ones

Cyclohexenones, which are relatively readily available as a result of a wide variety of condensation and cyclisation reactions, are the most common and apparently some of the most promising starting materials in the synthesis of substituted cyclohexa-1,3-dienes. The main schemes of such syntheses are as follows:



The frequent use of these schemes is due to the fact that their main disadvantage (inhomogeneity of the dienes obtained) was discovered only towards the beginning of the 1960's after the development of the chromotographic and spectroscopic analytical techniques.

(a) *Synthesis via secondary alcohols.* The literature data on the reduction of cyclohexenones and the dehydration of the unsaturated alcohols formed are presented in Table 1. The reductant employed is mainly lithium tetrahydroaluminate in boiling ether[2,21,80,82,85]; the yield of alcohols is 70–90%. The allyl alcohols formed are thermally stable and are readily purified by distillation.

The main method for the industrial dehydration of the enol (XXV) itself considered in the literature involves the passage of its vapour over alumina[23,86–88] and the optimum yield of the diene (I) (up to 85%) can be achieved at 270 °C. It has been established[86] that the reaction is accompanied by the formation of cyclohexene, cyclohexane, and benzene, the latter being absent from the first portions of the catalytic reaction mixture[23]; the amount of impurities is 2–5% and increases with contact time. In order to diminish the role of side processes, it has been suggested[88] that the vapour of compound (XXV) be diluted with water; for the optimum molar component ratio of 2 : 1 respectively, the degree of conversion is 77% and the purity of the product is 99%. According to patent data[89,90], when a specially prepared catalyst based on alumina is used, it is possible to achieve a yield of 94% combined with a purity of diene (I) of 96.5% (the rest is cyclohexene).

It has been reported[91,92] that calcium and magnesium phosphates are effective catalysts of the vapour-phase dehydration of compound (XXV); at 250–280 °C and for a contact time of 18–30 s, the diene (I) can be obtained in 70–85% yield with a purity of 97–99% according to refractometric data, which is doubtful. The application of an aluminium boride catalyst for this purpose in a fluidised bed at 250–280 °C has been described[93] (yield up to 93%, purity according to GLC 99.3%, the residue consisting of 0.6% of benzene and 0.1% of cyclohexene).

The dehydration of substituted cyclohexenols over alumina at 300 °C [21] or 350 °C [85] has been described (yield approximately 60%); it must be supposed that the dienes formed under these conditions are contaminated by their disproportionaton products.

Table 1. Synthesis of cyclohexadienes via the reduction-dehydration of cyclohexen-1-ones.

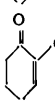
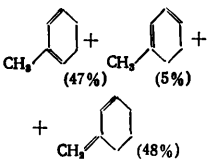
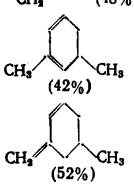
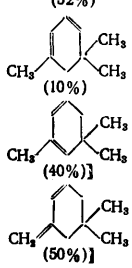
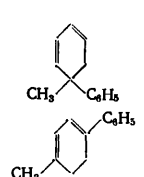
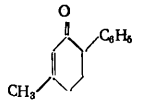
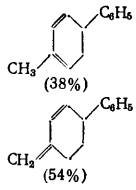
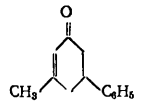
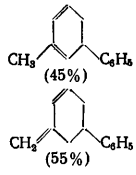
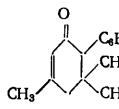
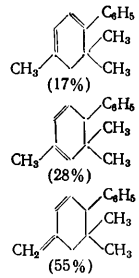
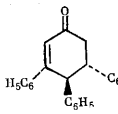
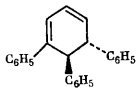
Initial ketone	Yield of alcohol, %	Dehydration conditions	Yield of hydrocarbon fraction, %	Composition of hydrocarbon fraction	References
	—	C	78		[79]
	89	*A*	80	 (96%)	[2]
	66	*A*	80	 (>99,5%)	[2]
	70	*A*	77	 (47%) (5%) (48%)	[2]
	—	C	—	 (42%) (52%)	[80]
	—	B	—	 (10%) (40%)] (50%)]	[80, 81]
	—	C	63		[79]
	—	C	58		[79]
	—	*A*	—	 (8%)	[82]

Table 1 (contd.)

Initial ketone	Yield of alcohol, %	Dehydration conditions	Yield of hydrocarbon fraction, %	Composition of hydrocarbon fraction.	Refs.
	—	B	—	 (38%) (54%)	[80]
	—	B	—	 (45%) (55%)	[80]
	—	B	—	 (17%) (28%) (55%)	[79, 83]
	—	D	65		[84]

* A = *p*-$CH_3C_6H_4SO_3H$; B = $CuSO_4$; C = $[(C_6H_3O)_3PCH_3]^+I^-$; D = $KHSO_4$.

Distillation of cyclohexenols in the presence of catalytic amounts of toluene-*p*-sulphonic acid[2,82], potassium hydrogen sulphate[94], magnesium chloride[75], or iodine[78] or refluxing with anhydrous copper or magnesium sulphate[95] has been widely used in laboratory practice for this purpose (Table 1). According to GLC data[2,80], the cyclohexadienes obtained by these methods are free of disproportionation products. The relatively low reaction temperature in this instance apparently makes it possible also to prevent the thermal isomerisation of the cyclohexa-1,3-dienes formed[2,80].

For the dehydration of cyclohexenols itself and 5,5-disubstituted cyclohexenols, it has recently been suggested[79,96] that the secondary alcohol be heated briefly at 50 °C with methyl triphenoxyphosphonium iodide in hexamethylphosphoramide; the dienes formed under these conditions in yields of 60–80% are free from impurities. However, in those cases where there is a possibility of different pathways in the elimination process, the reactions were not investigated.

Table 1 demonstrates the existence of different pathways in the dehydration of substituted cyclohexenols; in many cases the preferred reaction pathway is 1,4-elimination, which in the presence of an alkyl substituent in the 3-position leads to the formation of considerable (up to 40%) amounts of dienes with an exocyclic double bond. Homogeneous preparations can be obtained as a result of this reaction in only two cases:

(1) If any of the dehydration pathways leads to the same substance (this happens in the presence of one substituent in the 2-position or of two substituents in the 5-position, or of two identical substituents in the 2- and 5-positions).

(2) On geminal substitution in the 4,4- and 6,6-positions whereupon there is a possibility of only one reaction pathway.

Thus, despite its simplicity and convenience, this method of synthesis of substituted cyclohexadienes leads as a rule to mixtures of dienes (in the general case three-component mixtures) which are difficult to separate.

(b) *Synthesis via tertiary alcohols.* The interaction of cyclohexenones with organomagnesium and organolithium compounds followed by the dehydration of the tertiary unsaturated alcohols is apparently the most frequently employed method of synthesis of cyclohexadienes. The literature data on the application of this scheme are presented in Tables 2 and 3. In all the studies mentioned in the above tables, the organomagnesium compounds were synthesised and made to react with ketones in ether under standard conditions.

Attention should be drawn to the fact that the interaction of a Grignard reagent with cyclohexenones may be complicated by 1,4-addition which leads to saturated ketones[2,97]. This reaction lowers the yield of the dienes, sometimes to a considerable extent. With increase of the bulk of the substituent introduced into the molecule, the contribution of 1,4-addition increases sharply and can reach 70%;[97] copper(I) chloride catalyses this side reaction[97,124].

The tertiary alcohols formed as a result of the main reaction are as a rule unstable and are readily dehydrated, particularly in an acid medium. When the reaction mixture remaining after the organomagnesium synthesis is treated with acids (for example, with 6–10% sulphuric acid), the above alcohols cannot be isolated and the reaction products are diene hydrocarbons[104]. Traditional treatment of the reaction mixture with ammonium chloride also does not permit the isolation of the alcohols in many instances. Treatment with water makes it possible to isolate the alcohols only if the reaction mixture is poured into an ice–water mixture; the reverse order of mixing leads directly to the dienes[125]. The instability of the alcohols obtained complicates their purification and makes it desirable to dehydrate the residue after removing the ether from the hydrolysis products of the organomagnesium compounds (without drying the extract).

The dehydration of unsaturated tertiary alcohols can be achieved by their simple distillation (at 80–120 °C).[2] The addition of acid catalysts (oxalic[11] and toluene-*p*-sulphonic acids[2] and potassium hydrogen sulphate[118]) greatly accelerates the process, but the yield of dienes is then somewhat reduced. The composition of the dehydration products on distillation in a neutral medium and in the presence of toluene-*p*-sulphonic acid is virtually the same[2]. The application of phosphoryl chloride in pyridine for this purpose has been described[103] (yield 62%). The use of severe conditions, such as passing the vapour of the tertiary alcohol over alumina at 300 °C,[121] is evidently superfluous.

The composition of the mixtures of dienes obtained by the above procedure has been established reliably in an extremely limited number of cases[2,21,104,125]. In a number of studies the inhomogeneity of the product (the presence of an admixture of a diene with an exocyclic double bond) was suggested tentatively[106,109,117,118]. It has been postulated[109] that in some reactions the "transoid" dienes predominate in the mixtures produced. As a rule, the dienes obtained were regarded as homogeneous substances.

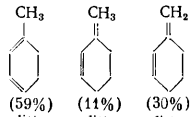
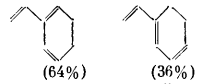
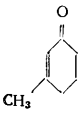
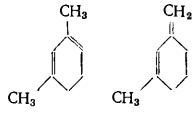
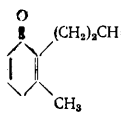
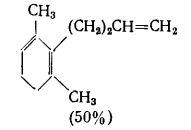
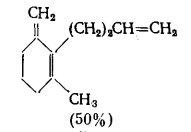
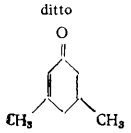
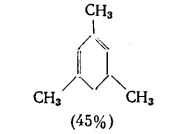
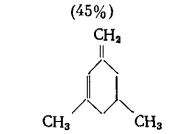
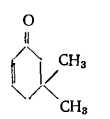
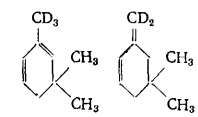
The data presented in Table 2 show that, when a methyl group is introduced by the given procedure into the molecule,

exceeds 30%. If a secondary alkyl group is introduced, such dienes are present in the mixture in still greater amounts. The presence of an alkyl substituent in the 3-position in the initial ketone increases the yield of the "transoid" diene to 45–55%.[3,21,104,125]. If the substituents in the 1- and 3-positions of the diene formed differ, the formation of two isomeric dienes with an exocyclic double bond is to be expected.

Finally, 1,4-elimination can lead to the appearance in the reaction products of a cyclohexadiene with a different disposition of the double bonds than would be expected from a formal inspection of the reaction scheme. This has been observed, for example, by Mironov et al.[2]

Thus the above reaction involving cyclohexadienes leads to complex mixtures of products and the literature data on this question contain numerous errors.

Table 2. Synthesis of cyclohexadienes from cyclohex-2-en-1-ones via organomagnesium and organolithium compounds (the composition of the reaction products has been established reliably).

Initial ketone	Reagent	Dehydration conditions	Yield, %	Mixture composition	Refs.
	CH_3MgI	*A*	69	 (59%) (11%) (30%)	[2,83, 97]
ditto	CH_3MgI	B	62	ditto (59%) ditto (12%) ditto (29%)	[2]
	$CH_2=CHMgBr$	*A*	—	 (64%) (36%)	[96]
ditto	$CH_2=CHMgBr$	C	<15	ditto (60%) ditto (40%)	[96]
	CH_3MgI	*A*	40	 (57%) (43%)	[98–103]
	CH_3MgI	*A*	—	 (50%)	[104]
				 (50%) ditto (50%) ditto (50%)	
ditto 	CH_3Li	*A*	—	ditto (50%)	[104]
	CH_3MgI	D	77	 (45%)	[21, 105–107]
				 (55%)	
	CD_3MgI	D	—	 (~50%) (~50%)	[80]

* A = distillation; B = p-$CH_3C_6H_4SO_3H$; C = $[(C_6H_5O).P(CH_3)_3]^+I^-$; D = $CuSO_4$.

Table 3. Synthesis of cyclohexadienes from cyclohex-2-en-1-ones via organomagnesium and organolithium compounds (the composition of the reaction products was postulated on the basis of the synthetic scheme).

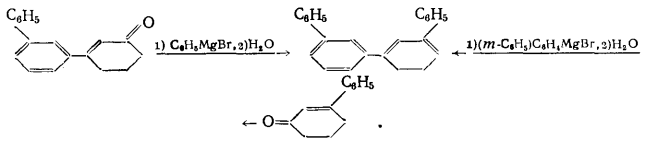
Substitution in initial ketone	Reagent	Dehydration conditions*	Yield, %	Refs.
Unsubstituted	C_6H_5MgBr	E	96	[13]
ditto	C_3F_7MgBr	E	43	[108]
3-Methyl-	C_2H_5MgBr	A	50	[109]
ditto	n-C_3H_7MgBr	A	50	[109]
ditto	iso-C_3H_7MgBr	A	19	[109]
ditto	n-C_4H_9MgBr	A	50	[109]
3-Ethyl-	C_2H_5MgBr	E	69	[110]
3-n-Butyl-	C_2H_5MgBr	E	83	[110]
ditto	n-C_4H_9MgBr	E	80	[110]
3-t-Butyl-	n-C_4H_9MgBr	E	80	[110]
4-Isopropyl-	CH_3MgI	F	70	[111]
4-(1,5-Dimethylhexyl)-	CH_3MgI	G	60	[112]
2-Phenyl-	C_6H_5Li	A	70	[113]
3-Phenyl-	$C_6H_{11}MgBr$	B	40	[114]
ditto	C_6H_5MgBr	E	~100	[14, 114]
ditto	p-$CH_3C_6H_4MgBr$	E	~50	[11]
ditto	$C_6H_5C_6H_4Li$**	E	~50	[115]
4-($CH_3C_6H_4$)-**	CH_3MgI	E	~50	[12]
3-(m-$C_6H_5C_6H_4$)-	C_6H_5Li	E	~50	[11]
ditto	m-$C_6H_5C_6H_4MgBr$	E	~50	[116]
3-(p-$C_6H_5C_6H_4$)-	m-$C_6H_5C_6H_4MgBr$	E	~50	[116]
5-Ethyl-3-methyl-	CH_3MgI	D	62	[106]
3-Methyl-5-n-propyl-	CH_3MgI	D	62	[117]
5-Isopropyl-3-methyl-	CH_3MgI	D	62	[117]
3,5-Diphenyl-	C_6H_5MgBr	E	80	[15, 115]
ditto	$CH_3C_6H_4MgBr$**	E	80	[15]
ditto	p-$C_6H_5C_6H_4Li$	E	—	[115]
5-Phenyl-3-m-tolyl-	p-$CH_3C_6H_4MgBr$	E	~80	[15]
5-Phenyl-3-p-tolyl-	p-$CH_3C_6H_4MgBr$	E	~80	[15, 102, 118–120]
ditto	C_2H_5MgBr	H	60	[121]
ditto	C_3H_7MgBr	H	60	[121]
ditto	$CH_2=CHMgBr$	A	70	[122]
ditto	$CH_3CH=CHMgBr$	A	70	[122]
3,4,6-Trimethyl-	CH_3MgI	A	70	[123]

*A = distillation; B = p-$CH_3C_6H_4SO_3H$; C = $[(C_6H_5O).P(CH_3)_3]^+I^-$; D = $CuSO_4$; E = 10% H_2SO_4; F = $(COOH)_2$; G = $POCl_3$ in C_5H_5N; H = $KHSO_4$.

** o-, m-, and p-isomers.

The isolation of the individual cyclohexadienes from the mixtures obtained requires the application of preparative GLC. 1,3-Diphenylcyclohexa-1,3-diene[14] (homogeneous according to the method of synthesis) and other polyphenylcyclohexadienes[11,12,115,116], which can be readily purified by crystallisation, are apparently and exception. However, one should bear in mind that in this case too it is difficult to predict unambiguously the positions of the double bonds in the diene obtained. For example, it is known[116] that the application of the above scheme in the examples quoted yields the same substance (the second isomer may be lost in the course

of the purification by crystallisation):



Furthermore, in analogous schemes[11], when one of the substituents is p-$C_6H_5C_6H_4$ and the other is C_6H_5, dienes with identical melting points are formed.

Thus, despite its wide-scale application, the method described is suitable only in a limited number of instances.

Table 4. Synthesis of cyclohexadienes via the tosyl hydrazones of substituted cyclohex-2-en-1-ones.

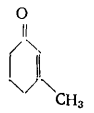
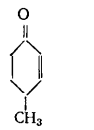
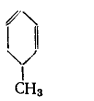
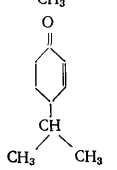
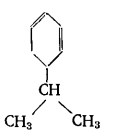
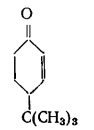
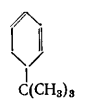
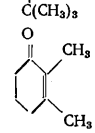
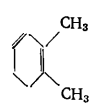
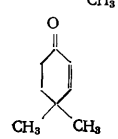
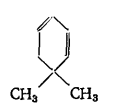
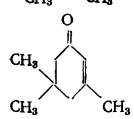
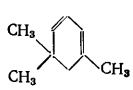
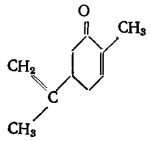
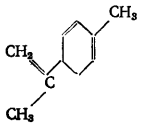
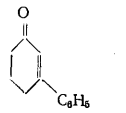
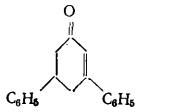
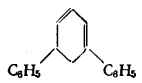
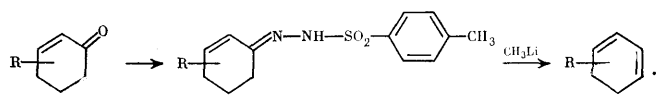
Initial ketone	Diene obtained	Yield, %	References
		50	[127]
		40	[127]
		—	[128]
		—	[128]
		—	[128]
		87	[126]
		85	[64, 126]
		~100	[126, 129]
		80	[126]

Table 4 (contd.)

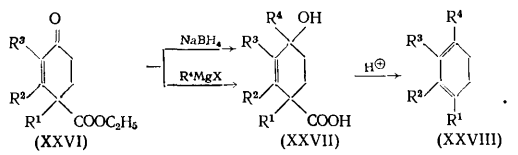
Initial ketone	Diene obtained	Yield, %	References
		40	[126]
		55	[126, 130—132]

(c) *Dauben's method.* In 1968 Dauben et al.[126] suggested that cyclohexenones be converted into cyclohexadienes by the reaction of the tosyl hydrazones of these ketones with methyl-lithium in a benzene–ether mixture; the literature data on this method are compiled in Table 4.



It has been reported[129] that in this process methyl-lithium can be replaced by n-butyl-lithium, but, according to Dauben et al.[126], such replacement results in a decrease in the yield of the diene and in addition the use of *n*-butyl-lithium results in the contamination of the diene produced by mono-olefinic compounds. A considerable advantage of the method under discussion is that hydrogen is eliminated exclusively from the α-position relative to the hydrazone group. In combination with the low temperature of the experiment, this makes it possible to obtain cyclohexadienes having a specified structure with a high degree of purity.

(d) *Plieninger's method.* A relatively convenient method of synthesis of substituted cyclohexadienes (XXVIII) involves the coupled dehydration–decarboxylation of 1-hydroxy-cyclohex-2-ene-4-carboxylic acids (XXIV):



(XXVI) (XXVII) (XXVIII)

The hydroxyacids (XXVII) are synthesised by the reduction of the relatively readily available ketoacid esters[16,133] with sodium tetrahydroborate in ethanol[16]; the dehydration-decarboxylation (as a rule without the isolation of the hydroxy-acids) is achieved on treatment of the acids with 4–5 *N* sulphuric acid at 20 °C. The overall yield of the dienes[16] is 14–60%. It has been suggested[134] that zinc tetrahydroborate in benzene be used as the reductant in the above scheme (yield of hydroxyacid 60–90%) and that the dineopentyl acetal of dimethylformamide be employed as the dehydrating agent at 20–70 °C in a non-polar solvent (α-methylnaphthalene), serving simultaneously as a "cushion" in the distillation of the diene. This procedure made it possible to increase the yield of dienes in the last stage to 50–85%. It is striking that this scheme yields dienes with a homogeneous isomeric composition free from extraneous impurities, which has been

shown convincingly[134]. The known instances of the application of this scheme are presented in Table 5. This is undoubtedly one of the promising methods of synthesis of substituted cyclohexadienes, but the conditions for the dehydration-decarboxylation of the hydroxyacids (XXVII) require further improvement; in particular the dehydrating agent (dineopentyl acetal of dimethylformamide) should be replaced by one more readily available.

Table 5. Synthesis of cyclohexa-1,3-dienes by the dehydration-decarboxylation of 1-hydroxycyclohex-2-ene-4-carboxylic acids.

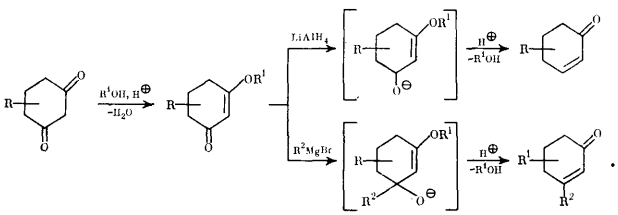
Substitution in initial ester (XXVI) (R^1–R^3) and in the diene (XXVIII) obtained				Reduction conditions	Yield of hydroxy-acids, %	Reaction conditions*	Yield of diene, %	References
R^1	R^2	R^3	R^4					
CH_3	H	H	H	$NaBH_4$	—	*A*	14**	[16]
CH_3	H	H	H	$Zn(BH_4)_2$	63	B	51	[134]
H	CH_3	H	H	$NaBH_4$	—	*A*	14**	[16]
H	CH_3	H	H	$Zn(BH_4)_2$	60	B	50	[134]
CH_3	CH_3	H	H	$NaBH_4$	86	*A*	85	[16]
CH_3	H	H	CH_3	CH_3MgI	64	B	54	[134]
H	CH_3	CH_3	H	$Zn(BH_4)_2$	94	B	84	[134]

* A = 5 *N* H_2SO_4, 20 °C; B = dineopentyl acetal of dimethylformamide.

** For two stages.

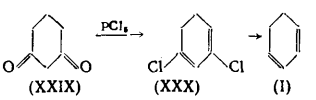
3. Synthesis from Cyclohexanediones and Cyclohexanediols

(a) *Starting materials.* The relatively readily available cyclohexane-1,3-diones in many instances serve as the starting materials for the synthesis of cyclohex-2-en-1-ones in accordance with the mechanisms (see, for example, Gannon and House[135]):



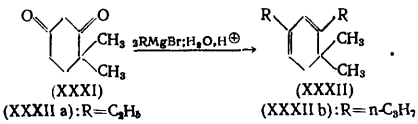
Cyclohexane-1,3-diols and cyclohexane-1,4-diols can be prepared by hydrogenating the corresponding diones or the available aromatic diols. Cyclohexane-1,2-diols are formed on oxidation of the corresponding cyclohexenes.

(b) *The substitution reaction.* When cyclohexane-1,3-dione is treated with phosphorus pentachloride in chloroform, it is possible to obtain 1,3-dichlorocyclohexa-1,3-diene (XXX) in approximately 60% yield, whose reduction with sodium in moist ether gives rise to the corresponding hydrocarbon containing an admixture of cyclohexene:



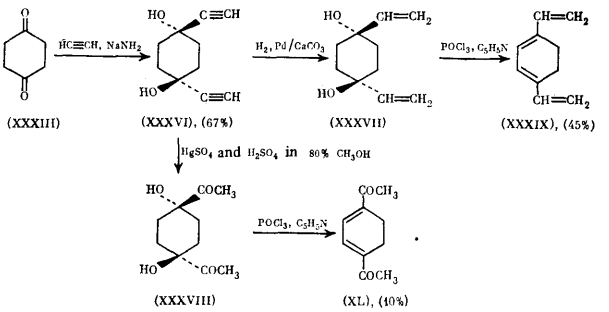
This reaction has also been described for 2-methyl-,[136] 5,5-dimethyl-, 5-phenyl-, and 2-methyl-5-phenyl-cyclohexane-1,3-diones. The yield of dichlorocyclohexadienes is 50–80%, but their purity has not been estimated.

(c) *Synthesis via tertiary alcoholds.* The interaction of hexanediones with two equivalents of a Grignard reagent followed by the dehydration of the resulting dione[137] leads to the diene fraction (XXXII) in approximately 50% yield;



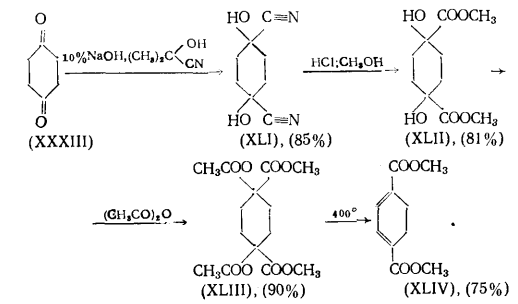
According to GLC data, the dienes formed are inhomogeneous, but the stretching vibration frequencies of the double bonds in the Raman spectra suggest that 1,3-dienes predominate in the mixtures. The synthesis of diphenylcyclohexadiene from cyclohexane-1,4-dione (XXXIII) has been achieved using an analogous scheme; organomagnesium synthesis under standard conditions led to a mixture of *cis*- and *trans*-1,4-diphenylcyclohexane-1,4-diols, whose dehydration with 20% sulphuric acid gave a 55% yield of 1,4-diphenylcyclohexa-1,3-diene (XXXIV), which was homogeneous according to the authors[138]. However, subsequent data[139] showed that the specimen contained 1,4-diphenylcyclohexa-1,4-diene (XXXV) (from 25 to 75% depending on the time of contact between the mixture of diols and the acid). Such mixtures are not susceptible to separation[139], but their treatment with potassium t-butoxide in t-butyl alcohol and subsequent crystallisation permit the isolation of the individual diene (XXXIV).

(d) *Synthesis via interaction with acetylides.* The interaction of dione (XXXIII) with sodium acetylide in liquid ammonia, leading to *trans*-1,4-diethynylcyclohexane-1,4-diol (XXXVI), from which divinylcyclohexa-1,3-diene (XXXIX) and diacetylcyclohexa-1,3-diene (XL) were obtained by means of the standard methods illustrated in the scheme below, has been described[140]:



1,4-Bis(2-phenylethyl)cyclohexadiene has been synthesised in accordance with an analogous scheme using phenylacetylene[141]. The positions of the double bonds in the dienes and also their homogeneity, which is particularly important for liquid divinylcyclohexadiene, have not been determined; it must be supposed that the preparations were not free from 1,4-isomers.

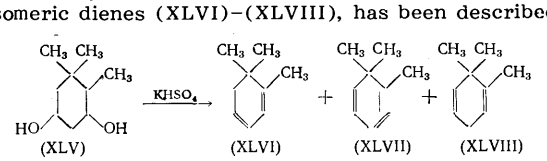
A related scheme has been used[142] to obtain dimethyl cyclohexadiene-1,4-dicarboxylate (XLIV):



A deficiency of this scheme is the use in the last pyrolytic stage of the diacetate (XLIII) at 400 °C, which is accompanied by a partial (18%) dehydrogenation of the substance. The homogeneity of the diene obtained relative to the positions of the double bonds has been confirmed by GLC data and the preparation of the adduct of the diene (XLIV) with maleic anhydride in a high yield. Evidently the given isomer predominates in the corresponding equilibrium mixture. The schemes presented above are not general and it is desirable to employ cyclohexanediones mainly for the synthesis of other starting materials—principally cyclohexenones.

(e) *Dehydration of cyclohexane-1,2-diols.* It has been shown by a large series of studies (see, for example, Refs. 143–145) that the dehydration of cyclohexane-1,2-diol cannot serve as a method of synthesis of cyclohexadiene, since its main products are cyclohexanone and formylcyclopentane. The synthesis of cyclohexane-1,2-diyl diacetate and its pyrolysis (540–660 °C) have been described[146] as a method of synthesis of cyclohexadiene, the yield in the last stage amounting to 84% according to the data presented[146]. However, the cyclohexadiene formed must be greatly contaminated by benzene. It is known that the products of the pyrolysis of 1-methylcyclohexane-1,2-diyl diacetate, obtained from 1-methylcyclohexene, contain a large amount of 3-methylenecyclohexene. Furthermore, the diene obtained should undergo isomerisation and aromatisation under the experimental conditions. Evidently the application of this extremely widely used scheme for the synthesis of dienes from monoolefinic compounds to the synthesis of cyclohexadienes is undesirable.

(f) *Dehydration of cyclohexane-1,3-diol.* The dehydration of cyclohexane-1,3-diol by 80% sulphuric acid gives rise to a mixture of cyclohexa-1,3-diene and cyclohexa-1,4-diene in proportions of approximately 5 : 1. The dehydration of *cis*-5,5-dimethylcyclohexane-1,3-diol[149,150] on distillation from phthalic anhydride leads to a 50% yield of 5,5-dimethylcyclohexa-1,3-diene, containing, according to GLC data, 8% of 3,3-dimethylcyclohexene and 8% of 4,4-dimethylcyclohexene, which can be readily removed by fractional distillation. Under the same conditions, *trans*-2,2-dimethylcyclohexane-1,3-diol[150] yields a complex mixture of products, which contains less than 10% of cyclohexadiene hydrocarbons. The dehydration of 5,5,6-trimethylcyclohexane-1,3-diol (XLV) on distillation with potassium hydrogen sulphate and resulting, according to Raman spectroscopic data, in a mixture of the isomeric dienes (XLVI)–(XLVIII), has been described[120]:



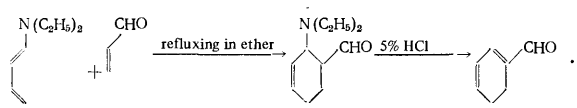
(g) *The elimination of water from cyclohexane-1,4-diol.* The elimination of water from cyclohexane-1,4-diol on treatment with 80% sulphuric acid gives a 44% yield of a mixture of cyclohexa-1,3-diene and cyclohexa-1,4-diene in proportions of 1 : 4. When the 1,4-diol is distilled from potassium hydrogen sulphate, the 1,4-isomer also predominates in the resulting mixture of dienes. The employment of anhydrous magnesium sulphate as the dehydrating agent[106] makes it possible to obtain a 40% yield of a mixture of dienes, in which the amount of the diene (I) is much greater. When cyclohexane-1,4-diol is distilled with phthalic anhydride (at 200 °C),[19] it is possible to obtain an 88% yield of a mixture consisting of 66% of the diene (I) and 34% of its 1,4-isomer according to GLC data. These mixtures can be readily separated by fractional distillation. Dehydration of cyclohexane-1,4-diol in a mixture with methanol in the vapour phase over alumina at 240–250 °C has been described[151]; the yield of the mixture of hydrocarbons was 48%. The main mixture component is apparently the diene (I), which has been isolated by column distillation and forms an adduct with maleic anhydride in a satisfactory yield.

The replacement of the dehydration of cyclohexane-1,4-diols by their conversion into diacetates with subsequent pyrolysis must be regarded as undesirable, since aromatisation takes place to a considerable extent (up to 28%) under the experimental conditions (450–500 °C).[152]

The data presented show that the synthesis of cyclohexa-1,3-dienes from cyclohexanediols leads as a rule to mixtures of the dienes and their 1,4-isomers.

4. Condensation and Cyclisation Reactions

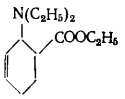
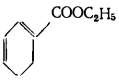
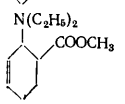
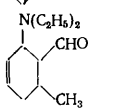
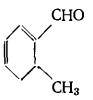
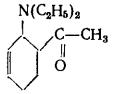
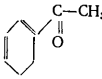
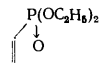
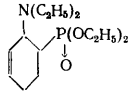
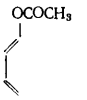
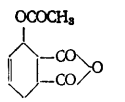
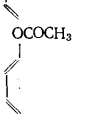
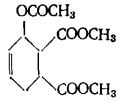
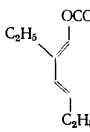
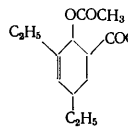
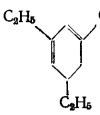
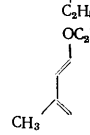
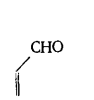
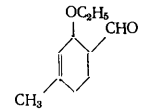
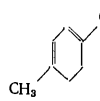
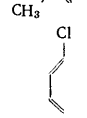
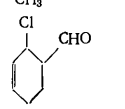
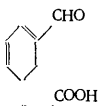
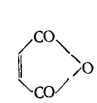
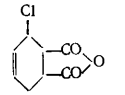
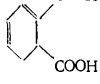
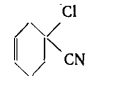
(a) *Diene condensation.* One of the preparatively important reactions for the formation of the cyclohexadiene ring is the diene condensation of acyclic dienes with dienophiles of the ethylene series when one of the addends (the diene or dienophile) contains a substituent which can be subsequently readily eliminated, for example[153]:



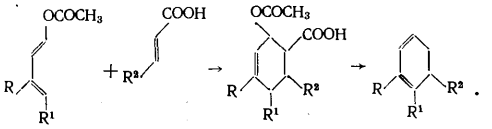
Examples of the employment of this scheme are compiled in Table 6. Dialkylamino-, acetoxy-, and alkoxy-groups, as well as the chlorine atom have been used as the substituents to be eliminated. The specific features of the diene condensation reaction limit the scope of the above scheme solely to the synthesis of cyclohexadienes containing electron-accepting groups, mainly carbonyl and carboxy-groups. The purity and the isomeric composition of the dienes obtained, described in Table 6, were in the vast majority of cases not determined. However, presumably the elimination took place preferentially via the pathway represented, since it corresponds to the elimination of the most mobile hydrogen atom from the α-position relative to the electron-accepting group, whereas the isomerisation of the dienes under the experimental conditions is unlikely.

It has been recently reported[168] that the diene condensation of 1-acetoxybuta-1,3-diene and its homologues with derivatives of acrylic and fumaric acids results in the formation of acetoxycyclohexene-carboxylic or dicarboxylic acids, which can be converted into the corresponding cyclohexa-1,3-dienes in 69–87% yield as a result of the elimination of

Table 6. Synthesis of cyclohexadienes via diene condensation-elimination.

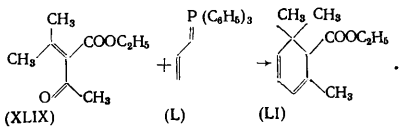
Diene	Dienophile	Adduct	Eliminated molecule	Elimination conditions	Yield, %	Cyclodiene	References
			$HN(C_2H_5)_2$	5% HCl	40		[153]
ditto			ditto	HCl in C_2H_5OH	58		[154—158]
ditto			ditto	ditto	42		[159]
ditto			ditto	10% HCl	16		[153]
ditto			ditto	heating	<20		[153]
ditto			ditto	NaH	~30		[160]
			CH_3COOH	HCl	~60		[161—163]
			ditto	4% KOH	<20		[162]
			ditto	heating	30		[164]
			C_2H_5OH	heating	80		[165]
	ditto		HCl	heating	~80		[166]
ditto			ditto	KOH in CH_3OH	—		[167]
			»	$(CH_3)_3COK$	—		[24]

acetic acid and decarboxylation:



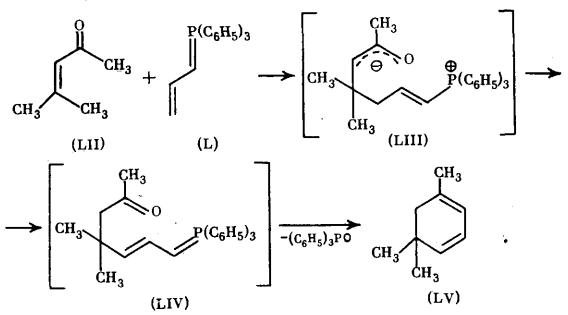
Unfortunately specific methods are not described in the above communication[168]: nor are there any data concerning the positions of the double bonds in the dienes formed.

(b) *Intramolecular Wittig reaction.* It has been observed [169] that, instead of the expected product of the Wittig condensation, the interaction of allylidenetriphenylphosphorane (L) with the ketoester (XLIX) gives rise to a 60% yield of compound (LI) with a cyclohexadiene ring:



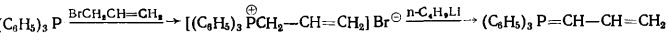
(XLIX) (L) (LI)

This method is general for the synthesis of substituted cyclohexa-1,3-dienes[169,170]:



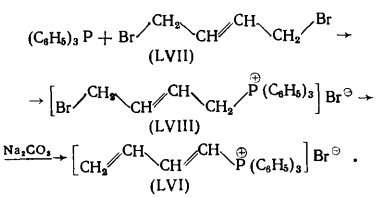
(LII) (L) (LIII) (LIV) (LV)

This reaction[170] involves the addition of the ylide (L) to the β-position of the unsaturated ketone (LII) with formation of a structure of type (LIII). Proton transfer leads to the ylide (LIV), which is capable of undergoing the intramolecular Wittig condensation. The reaction proceeds under mild conditions and makes it possible to obtain dienes in 30–60% yield. The initial ylide of type (L) is synthesised by the reduction of the corresponding phosphonium bromide with n-butyl-lithium:



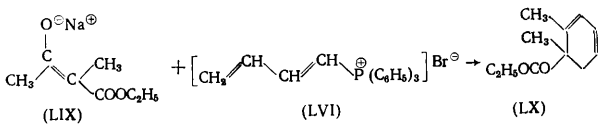
According to Büchi and Wüest[169] and Dauben et al.[170], the reaction is not accompanied by any side processes and makes it possible to obtain homogeneous preparations of cyclohexa-1,3-dienes. Examples of the application of this reaction are presented in Table 7.

The condensation of *trans*-1-butadienylphenylphosphonium bromide (LVI) with the enolates of carbonyl compounds is a convenient method of synthesis of cyclohexadienes[171–173]. The salt (LVI) can be obtained in a high yield (92%) on interaction of triphenylphosphine with *trans*-1,4-dibromobut-2-ene (LVII) in benzene with subsequent dehydrobromination of the resulting *trans*-4-bromobut-2-enyltriphenylphosphonium bromide (LVIII) by anhydrous sodium carbonate in chloroform:



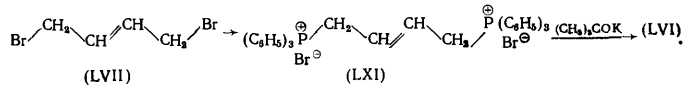
(LVII) (LVIII) (LVI)

When the salt (LVI) is refluxed with carbonyl compounds in the form of enolates (LIX) in tetrahydrofuran, cyclohexa-1,3-dienes (LX) are formed:



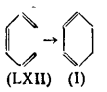
(LIX) (LVI) (LX)

Examples of the use of this reaction are presented in Table 8. The method under discussion leads to highly pure dienes. The interaction of the diphosphonium salt (LXI) with potassium t-butoxide in ether also leads to the salt (LVI), which condenses with carbonyl compounds under the experimental conditions giving rise to cyclohexadienes in high yields[171]:



(LVII) (LXI)

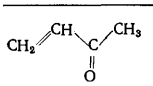
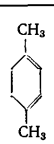
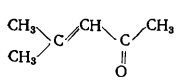
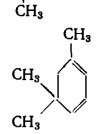
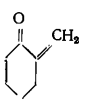
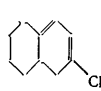
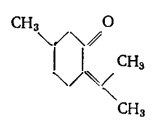
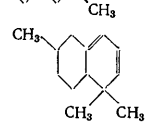
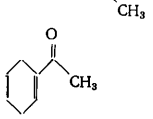
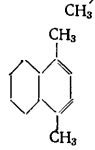
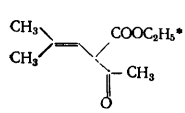
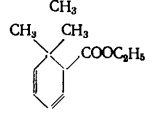
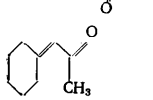
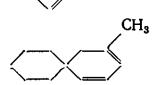
(c) *Electrocyclisation of hexa-1, 3, 5-trienes.* It is known that the thermal cyclisation of 3-*cis*-hexa-1,3,5-trienes leads to compounds of the cyclohexadiene series:



(LXII) (I)

The literature data for this reaction are compiled in Table 9. The reaction is typical electrocyclisation which proceeds strictly stereoselectively[185–187] via a disrotatory pathway. Only the 3-*cis*-trienes undergo the cyclisation reaction below 230 °C; their 3-*trans*-isomers are thermally stable below this temperature[184–188]. The potential barrier to the conversion of 3-*trans*-trienes into the *cis*-isomers is 41–51 kcal mol^{-1}.[188,189]

Table 7. Synthesis of cyclohexadienes by the condensation of α, β-unsaturated ketones with allylidenephosphoranes[170].

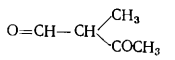
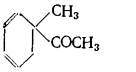
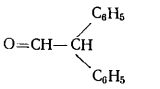
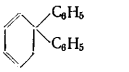
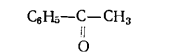
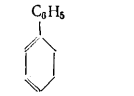
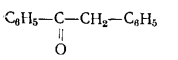
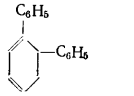
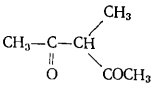
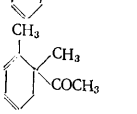
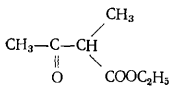
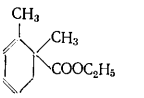
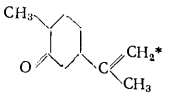
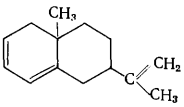
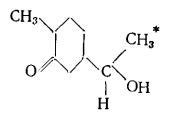
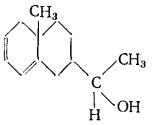
Unsaturated ketone	Yield*	Diene obtained	Reaction conditions	Yield, %
	B		ether, 25° 30 h	62
	A		ether, 25°, 30 h	55
	B		THF, 25°, 18 h	25
	A		THF, 25°, 16 h	41
	B		THF, refluxing, 30 h	25
	A		ether, 25°, 14 h	60
	A		ether, 25°, 12 h	32

* A = $CH_2=CH-CH=P(C_6H_5)_3$; B = $CH_3-CH=CH-CH=P(C_6H_5)_3$.

** See Büchi and Wüest[169].

Under mild conditions (100–170 °C), the reaction is not accompanied by the formation of side products. However, despite the simplicity with which it can be carried out, the cyclisation of *cis*-hexa-1,3,5-trienes has no preparative value at the present time because of the low availability of the pure 3-*cis*-trienes, whose synthesis usually leads to their mixtures with the *trans*-isomers. The employment of such mixtures precludes the preparation of homogeneous cyclohexa-1,3-dienes.

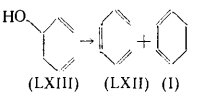
Table 8. Synthesis of cyclohexadienes by the reaction of the enolates of carbonyl compounds with *trans*-1-butadienyltriphenylphosphine bromide[171].

Initial ketone or aldehyde	Reaction product	Yield, %
		35
		35
		45
		57
		40
		57
		85
		73

* See Büchi and Pawlak[172].

It has been reported[190,191] that the cyclisation reaction of hexa-1,3,5-trienes is catalysed by alumina, but the use of this catalyst cannot be regarded as desirable, since the reaction products are inevitably contaminated by aromatic compounds.

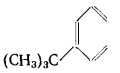
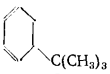
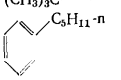
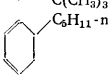
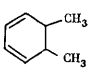
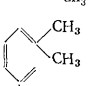
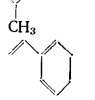
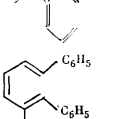
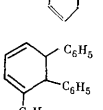
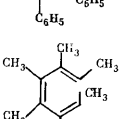
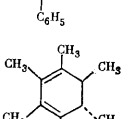
Many synthetic methods designed to obtain hexa-1,3,5-trienes lead directly to cyclohexadienes. Thus the dehydration of hexa-1,5-dien-3-ol (LXII) with phthalic anhydride results in the formation of the diene (I) (30%) together with the hexatriene (LXII) (70%):



(LXIII) (LXII) (I)

The cyclodehydration of substituted hexa-3,5-dien-2-ols also takes place under the influence of alumina at 200–500 °C. However, the cyclohexadienes obtained under such conditions[9,179,180,192,193] undergo aromatisation to a large extent (up to 80%)[179].

Table 9. Thermal cyclisation of hexa-1,3,5-trienes.

Initial triene	*t*, °C	Product	Yield, %	Thermodynamic parameters $\Delta H^{\neq}$, kcal mol^{-1}	Thermodynamic parameters $\Delta S^{\neq}$, e.u.	Refs.
	120—190		100	29.3	—7.3	[174—178]
	100—150		—	28.9	—4.9	[179—181]
	100—150		—	26.1	—12.4	[179—181]
	100—150		100	27.0	—6.2	[181]
	100—150		100	26.0	—11.3	[181]
	75—125		100	26.7	—11.3	[181]
	110—150		100	27.8	—7.9	[182]
	132		100	29.4	—7.0	[183]
	120—170		100	31.8	—13.8	[184]
	84—122		100	22.0	—13.8	[96]
	150		65	—	—	[84]
	210		98	27.4	—19.0	[185]

Thus, among the numerous condensation and cyclisation reactions leading to compounds of the cyclohexa-1,3-diene series, the synthesis via organophosphorus compounds and

the diene condensation of acyclic compounds with subsequent elimination of a substituent may be of preparative value. The latter reaction cannot, however, be regarded as a general method of synthesis of cyclohexa-1,3-dienes.

5. Other Methods

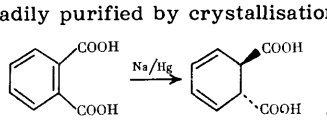
Among the numerous other reactions whose products are cyclohexa-1,3-dienes, only a few are of preparative importance. The isomerisation of cyclohexa-1,4-dienes, the synthesis of acids of the cyclohexadiene series, and also the transformation of substituents in the complete cyclohexa-1,3-diene ring can be included among them.

(a) *Isomerisation of cyclohexa-1,4-dienes.* Cyclohexa-1,4-dienes are obtained by the reduction of aromatic compounds with an alkali metal (usually sodium) and alcohol in liquid ammonia; despite the large bibliography on this reaction, we shall confine ourselves to mentioning only the first communication[194] and two reviews[195,196]. The most convenient recipe for the preparation of cyclohexa-1,4-diene itself was given by Wibaut and Hoak[197]. Cyclohexa-1,4-dienes containing electron-accepting groups (for example, the carbonyl or carboxy-groups) are available as a result of the diene condensation of buta-1,3-dienes with acetylenic dienophiles (see, for example, Onishchenko[198]).

It has been reported that the transformation of cyclohexa-1,4-diene into the 1,3-isomer (I) is possible on treatment with alkali metal alkoxides (in liquid ammonia[199,200] or in dimethylformamide[201]) or with potassium amide[202]. However, one should bear in mind that this transformation is reversible and that the ratio of the dienes in the resulting mixture depends significantly on the nature of the base and the solvent as well as other reaction conditions (see, for example, Mironov et al.[8]). One cannot rule out the possibility that the isomerisation of cyclohexa-1,4-diene in the presence of sodium ethoxide in liquid ammonia (in the absence of a proton donor from the reaction mixture) can serve as the basis of the industrial manufacture of the diene (I), provided that the admixture of the 1,4-isomer and benzene do not interfere with its subsequent employment.

The reduction of aromatic compounds with subsequent isomerisation of the resulting cyclohexa-1,4-diene has been described as a method of synthesis of substituted cyclohexa-1,3-dienes in relation to toluene[202,203], *p*-xylene[203], anisole [204–206], 1-methoxy-3,4-dimethylbenzene[205], 1-dimethylamino-4-methylbenzene[207], and biphenyl[208]. The isomerisation reaction has been carried out mainly under the influence of sodium amide in liquid ammonia and the yield has been as a rule high, but in some instances[206] the reversibility of the reaction has been noted.

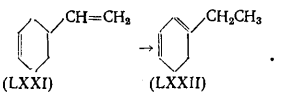
(b) *The Baeyer method.* Among the transformations of aromatic compounds into cyclohexa-1,3-dienes, one of the most convenient involves the reduction of phthalic acid (LXIX) (more precisely its sodium salt) with 3% sodium amalgam by the Baeyer method, which leads to a 60% yield of *trans*-cyclohexa-3,5-diene-1,2-dicarboxylic acid (LXX), which can be readily purified by crystallisation:



(LXIX) (LXX)

It has been reported[209] that the transformation of compound (LXIX) into compound (LXX) can be achieved by electrochemical reduction at a lead cathode in 99% yield. One should bear in mind that, on being refluxed in aqueous solution, the acid (LXX) isomerises quantitatively to cyclohexa-2,4-diene-1,2-dicarboxylic acid[210,211].

(c) *Isomerisation of 4-vinylcyclohexene.* The isomerisation of the readily available 4-vinylcyclohex-1-ene (LXXI) (dimer of buta-1,3-diene) has been used as a method of synthesis of 1-ethylcyclohexa-1,3-diene (LXXII):

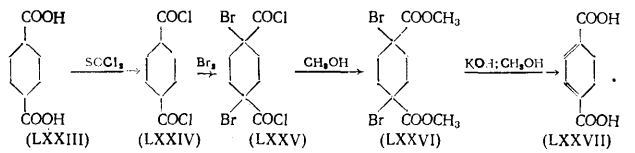


(LXXI) (LXXII)

When the diene (LXXI) is passed over alumina at 350 °C, the yield of the diene (LXXII) is 60% [212,213]; according to GLC data, the substance contains a large number of small amounts of side products. However, it is extremely unlikely that the diene (LXXII) obtained under these conditions did not contain considerable admixtures of ethylbenzene and the 2-isomer.

Cobaltocene has been used as the catalyst of this reaction [214] (15 h at 185 °C). Presumably, under these fairly mild conditions, the substance obtained is more homogeneous, but its yield is low (23%).

(d) *Synthesis of cyclohexa-1,5-diene-1,4-dicarboxylic acid.* The following scheme has been widely used to synthesise cyclohexa-1,3-diene-1,4-dicarboxylic acid (LXXVII)[210, 215–217]:



(LXXIII) (LXXIV) (LXXV) (LXXVI) (LXXVII)

The interaction of the acid (LXXIII) with thionyl chloride at its boiling point leads to the acid dichloride ((LXXIV). Bromination of the latter (without isolation in a pure form) at room temperature and subsequent refluxing with methanol give rise to a mixture of the *cis*- and *trans*-isomers of the dibromoester (LXXVI). Crystallisation makes it possible to isolate in 44% yield the homogeneous *trans*-isomer of compound (LXXVI)#.[217] The dehydrobromination of the *trans*-dibromoester (LXXVI) by refluxing it with a solution of potassium hydroxide in methanol leads to an almost quantitative yield of the acid (LXXVII), which can be readily purified by crystallisation. Despite the large number of stages, the required product can be obtained in a satisfactory yield.

(e) *Transformation of substituents in the cyclohexa-1,3-diene ring.* The transformation of substituents in the complete cyclohexa-1,3-diene ring is represented by a limited number of examples and standard synthetic methods are used as a rule: esterification of carboxylic acids[210,215,217,218] (yield 70–80%), hydrolysis of the acid esters[219], conversion of cyclohexa-3,5-diene-1,2-dicarboxylic acid into the corresponding anhydride[163], and the reduction of esters of substituted cyclohexa-1,3,5-diene-1,2-dicarboxylic acid with lithium tetrahydroaluminate to the corresponding diols (yield 70 to 80%); [220,221] by reduction with lithium tetrahydroaluminate, the diols were re-reduced with lithium tetrahydroaluminate

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The isolation of the residual reaction products[215] is apparently undesirable, since the resulting mixture contains dimethyl terephthalate.

via their toluene-p-sulphonates or methanesulphonates into hydrocarbons with two methyl groups in yields up to 80% [220, 221]. Thus the majority of the reactive groups in cyclohexa-1,3-dienes can be transformed without affecting the diene ring.

IV. CONCLUSION

Inspection of the synthetic methods described above for cyclohexa-1,3-dienes reveals the following features.

The method involving the bromination-dehydrobromination of cyclohexene is most convenient for the laboratory synthesis of cyclohexa-1,3-diene itself. The Hofmann–Damm method makes it possible to obtain a fairly homogeneous preparation. The much simpler method involving the dehydrobromination of dibromocyclohexane with quinoline or alkoxides can be recommended in those cases where the presence of cyclohexene and benzene in the resulting preparation does not interfere with subsequent reactions.

The majority of the methods of synthesis of substituted cyclohexadienes described in the literature must be regarded as satisfactory. Thus the commonest schemes in which the starting materials are cyclohexenes, cyclohexanediones, cyclohexenones, and cyclohexanediols as a rule give rise to complex mixtures of hydrocarbons where the diene which should be formally the product of the given reaction may be present in only insignificant amounts.

Among the general methods of preparative synthesis of pure substituted cyclohexadienes, the most important are as follows:

(a) Interaction of cyclohexenone tosylhydrazones with lithium alkyls.

(b) The coupled dehydration-carboxylation of 1-hydroxycyclohex-2-ene-4-carboxylic acids.

(c) The condensation of organophosphorus compounds with unsaturated ketones or the enolates of saturated ketones.

Cyclohexadienes containing electron-accepting groups can be most readily obtained by the diene condensation of acyclic dienes followed by the elimination of the functional group present in the diene or the dienophile. Many of the other methods described make it possible to obtain in specific individual instances substituted cyclohexa-1,3-dienes in satisfactory yields and with a high purity, but such instances constitute an exception rather than the rule for the schemes considered.

The method involving the oxidation of cyclohexene by atmospheric oxygen and the dehydration of the resulting cyclohexenol is at present most completely prepared for industrial application. Despite the relatively low yield of the oxidation product in a single cycle (15–30%), the possibility of the ready regeneration of the unreacted cyclohexene permits the attainment of its conversion into cyclohexenol up to 70%. The conditions for the dehydration of the latter have been fairly thoroughly determined. This and the other stage can serve as the basis of a continuous process. One cannot rule out the possibility that the chlorination of cyclohexene and the subsequent dehydrochlorination of dichlorocyclohexene or 3-chlorohexene may prove economically more effective but this method has been less thoroughly investigated compared with that described above.

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Complementation Interactions of Oligonucleotides

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The results of studies by NMR, ultraviolet spectroscopy, circular dichroism, and X-ray diffraction of complexes of complementary oligonucleotides containing between two and fifteen monomeric units are surveyed. The review deals with the structures of the complexes in solution and in the crystalline state and the thermodynamics (using different theoretical models) and kinetics of their formation. The influence of the nucleotide composition and of the sequence and length of the oligomers on the structure and properties of the complexes as well as the biological importance of these systems are discussed. Attention has been devoted to the question of the stability of individual pairs of nucleotide complexes as a function of their nature and position in the oligomer chain.
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I. INTRODUCTION

The complementary complexes of synthetic poly(oligo)nucleotides are widely used as models of fragments of nucleic acids (NA) for the solution of many problems in molecular biology. The thermodynamic and kinetic aspects of the formation of complementary pairs, necessary for the understanding of any processes involving the breakdown and formation of double helices, are investigated with their aid. The role of nucleotide complexes has been increasing in the study of the protein–nucleic acid interactions, of the mechanism of the action of enzymes in nucleic acid metabolism, etc. The complexes of oligodeoxyribonucleotides, containing sequences which are split by restriction enzymes, recently found a new application—for the construction of recombinant DNA molecules. They serve as linkers in the addition of a natural or synthetic DNA molecule to the cloning vector or as adaptors with the aid of which additional restriction sites as well as DNA fragments, for example the initiating and terminating codons, the Shine–Delgarno sequence, etc. are built into the recombinant molecules.

Previously homopolynucleotides and polymers with repeating di(tri)nucleotide sequences mainly served as models of nucleic acids. Recently, in connection with considerable advances in synthetic nucleotide chemistry and development of methods of genetic engineering, complexes of oligo(poly)nucleotides with heterogeneous sequences have become available. Complexes of short nucleotides are used on a particularly wide scale. They make it possible to alter specifically the length of double helix sections and to vary the nucleotide sequence. Since short oligonucleotide complexes readily dissociate in aqueous buffer solutions at moderate temperatures, it is convenient to investigate with their aid any properties associated with the breakdown of double helix structures and the thermodynamic description of such systems can be based on simpler models. Oligomeric systems make it possible to investigate the influence of the length of the double helix section and of the nucleotide sequence on the thermodynamic and kinetic parameters of the complex formation as well as the optical properties of the double helices. Oligomeric systems are the most convenient objects for the elucidation of the kinetics of the formation of complementary complexes and of the influence of "error" bases on the stability and structure of the double helices.

Several reviews, constituting chapters of monographs and textbooks in English, have been devoted to the problems of the interaction of complementary oligonucleotides[1–4]. Riesner and Römer[1] discuss mainly theoretical aspects of the complex formation and the theory of the formation of "hairpin" structures. Ts'o's review[2] (1974) is devoted mainly to the consideration of complexes with non-canonical pairs of bases—the self-associated species oligo(A) [U, C, or G]. The review of Cantor and Schimmel[3] deals with the statistical thermodynamics and kinetics of the formation of duplexes by oligoribonucleotides (including mainly the hairpin and loop structures) and the employment of such data for the prediction of the secondary structure RNA as well as the kinetics of the denaturation and renaturation of DNA. The results of the crystallographic study of short oligomeric duplexes are discussed in Seeman's review[4]. In addition, the complexes of oligonucleotides are mentioned in reviews and other topics: on the interaction of mono(oligo)nucleotides with polynucleotides[5]; on the structure of RNA[6]; on the study of polynucleotides[7] and single-stranded oligonucleotides by NMR[8]. The present review embraces virtually all the aspects of the complex formation by oligonucleotides containing from 2 to 15 monomeric units (including studies up to 1981). Particular attention has been devoted to the results obtained in recent years in the study of the interaction of oligonucleotides by NMR and data on the structure of the oligomeric duplexes. The review does not discuss in detail studies dealing with the formation of "hairpin" structures and complexes of oligonucleotides containing non-complementary bases.

II. TYPES OF OLIGOMERIC COMPLEXES INVESTIGATED

The oligomeric complexes can be formed by oligonucleotides of identical or different lengths with complementary sequences or by self-complementary oligonucleotides. Depending on the nucleotide sequence and the chain length in these systems, the formation of several types of complexes has been noted.

Complexes of the readily available synthetic oligoribonucleotides with a homogeneous composition have been investigated most completely: oligo(A).oligo(U)[9–11] [the complexes oligo(G).oligo(C) have not been investigated hitherto]. Oligomers with a homogeneous sequence tend to form triple-stranded helices capable of coalescing into aggregates of the "concatameric" type with a higher molecular weight (see below)[9,11]. When the short oligomers of adenylic and uridylic acids interact, the stoichiometry of the complexes remains 1A:2U regardless of the chosen conditions[9]. It has been demonstrated[11] that the chain length of the oligomers, i.e. the number of monomeric units involved in the complementation interactions (N) above which there is a possibility of the formation of double helices, is seven. Systems incorporating oligodeoxyribonucleotides form as a rule double-stranded helices[12]. Thus the hybrid oligomeric complex $d(pT)_8.r[A(pA)_7]$ has the stoichiometry 1T:1A in a neutral buffer containing 1 M NaCl.[13] A double helix structure is also characteristic of a complex of oligodeoxyribonucleotides of different lengths: $d(pT)_{12}.d(pA)_6$.[14]

Oligomers with an alternating self-complementary nucleotide sequence usually form either intermolecular double helical complexes, such as, for example, oligo [d(pGG–C)] with a chain length ranging from 4 to 7 monomeric units[15], or intramolecular complexes as a result of the folding of the oligomer chain: $d(A–T)_n$ ($n > 7$).[16] The particular structure of the complex is apparently determined by the length of the oligomer. In the formation of complexes by oligonucleotides of different lengths with alternating non-complementary bases, namely oligo[d(C–A)].oligo[d(T–G)],[17] as well as trinucleotides and oligomers containing repeating trinucleotide sequences, namely d(pG–G–T).$d(pA–C–C)_{2-4}$, etc.,[18] the formation of double helix structures with continuous filling of the matrix by shorter oligomers is favoured.

Detailed study of the structural characteristics of the complexes of self-complementary block copolymers $(Ap)_mApU(pU)_n$[19] revealed a dependence of the structure of the complexes on the A/U ratio in the oligomer chain. A double-stranded helix is formed for $m \geq n$, while larger aggregates containing triple-stranded sections are produced for $m < n$.

The interaction of oligonucleotides with a heterogeneous nucleotide sequence leads to the formation of short double helix duplexes with a fixed position of one nucleotide chain relative to the other[21–26], provided that such interaction is not complicated by the self-aggregation of the components, as in the case of the complex G–G–C.G–C–C.[20] It has been observed recently that the hybrid ribo-deoxyriboduplex $r(C–U_5–G).d(C–A_5–C)$ has a triple helix (2:1) structure[27].

If the primary structures of the heterogeneous oligomers permit the formation of duplexes with "sticky" ends, for example, d(G–A–T–C–C–G–A–A–T–T–C–G)[28], d(T–G–C–A–C–A–T–G)[29], d(T–G–G–C–C–A–A–G–C–Tp)[30,31], and $d(A–T)_3(C–G)_3$,[32] etc.,[33] then the self-association of such oligomers results in the formation of double helices of the "concatameric" type. Concatamers are double helix complexes containing repeating nucleotide sequences. The structure of the concatamers formed by the above oligonucleotides resembles that of the polymeric complexes but differs from it by the presence of non-coincident breaks in the complementary chains.

III. THERMODYNAMIC DESCRIPTION OF THE COMPLEX FORMATION BY COMPLEMENTARY OLIGONUCLEOTIDES

1. General Principles of the Cooperative Interaction of the Oligomers

According to modern ideas, the characteristics of the behaviour of double (triple) helix nucleotide structures in solution are determined by the interaction between the heterocyclic bases, the influence of the solvent, and the electrostatic effects of the phosphate groups. The forces involved in the complex formation have been considered theoretically in a monograph[34]. The change in the state of each covalently bound monomeric unit in the complementary complex does not take place independently of the neighbouring units, which is the reason for the cooperative character of the formation and dissociation of the double (triple) helix systems. The compact packing of the heterocyclic bases of the double helix is drastically impaired in the dissociation of the complex, which is reflected in the cooperative alteration of many physicochemical characteristics of the system[5]—the absorption ultraviolet and infrared spectra, the circular dichroism (CD) and optical rotatory dispersion (ORD) parameters, NMR signals, and also hydrodynamic parameters, etc. The curves for the temperature variation of these parameters are referred to as the melting curves and make it possible to estimate the fraction of paired bases (f) at a given temperature. For example[19]:

$$f(T) = \frac{A_s(T) - A(T)}{A_s(T) - A_d(T)},$$

where $A_S(T)$ and $A_d(T)$ are the ultraviolet absorbances of the denatured and native complexes respectively at the given temperature, $A(T)$ is the ultraviolet absorbance of the solution observed at the given temperature (a point on the melting curve—Fig.1). T_m is defined as the temperature at which $f = 1/2$.

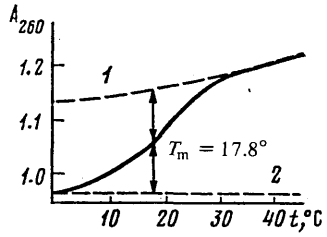
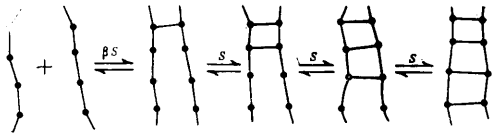


Figure 1. Temperature variation of the optical density of the intermolecular complex formed by $(Ap)_4ApU(pU)_4$ (1 M NaCl, pH 7.4): 1) $A_S(T)$; 2) $A_d(T)$.[19]

The statistical theory of the helix–coil transition, based on a modified monomeric Ising model[35], has now been fairly thoroughly developed[36] and is used to obtain the thermodynamic parameters of the complex formation process from the analysis of the experimental melting curves. Within the framework of this theory, the cooperative properties of the complementary oligomeric complexes, incorporating a single type of base pairs, can be described by a simple model with three parameters: the nucleation parameter β of the double helix ($\beta \ll 1$); the equilibrium constant S of the formation of the nucleotide pair next to a double helix sequence already

formed ($S > 1$); the number N of base pairs in the duplex. According to Applequist and Damle[37], the formation of the helix can be represented schematically as follows for the tetramer:



where βS is the formation constant of the isolated base pair (it determines the helix initiation process). The essential feature of the theory consists in the fact that the base pairs within the structure are much more stable than the terminal pairs and the initiation of the double helix therefore leads to the rapid complementary pairing of the bases of the entire nucleotide chain. However, the free energy gain for fairly long nucleotide sequences, which determines the increase in the length of the double helix, is compensated by the favourable entropy characteristics of the incompletely bound structures. The statistical weight of such structures increases sharply with increasing chain length. Indeed, whereas the formation of a complete double helical complex or a fully dissociated coil can occur in only one way, one can imagine a multiplicity of intermediate structures containing half of the theoretically possible nucleotide pairs. The competition between the above two factors leads to a finite average length L of the helical segments, in the region of the helix–coil transition, alternating with the melted sections; $L \cong 20$–100 nucleotide residues[1]. In the case of fairly short oligomeric sequences, with $N \ll L$, the complex formation process can be described with the aid of the "all or nothing" model (the two-state model), neglecting the number of oligonucleotides in which not all the bases are linked within the complex.

2. The Two State Model

Complex formation in accordance with the "all or nothing" principle takes place for fairly large helix propagation constants $S > 10$ (Pörschke[11]) ($\beta \ll 1$). Within the framework of this model, it is assumed that in the range of the helix–coil transition short or even nucleotides exist in only two states—in the fully double helix state or in the free state. The equilibrium constant K for the complex formation by the oligonucleotides containing N monomeric units can be formulated as the product of the constants for the individual stages of the reaction[15]:

$$K = \beta S^N \ .$$

The equilibrium constant can also be expressed in terms of f (Borer et al.[23]):

$K = f/2(1-f)^2c$ (interaction of self-complementary chains);

$K = 2f/(1-f)^2c$ (interaction of non-identical complementary sequences of the same length),

where c is the overall nucleotide concentration of the oligomeric components.

The equilibrium constant of the interaction of trinucleotides with complementary oligomeric matrices, containing repeating trinucleotide sequences[18], as well as the equilibrium constant of the formation reaction of concatamers with symmetrically overlapping blocks[29] were derived recently. The fraction of paired bases can be determined directly with the aid of osmometric experiments. A more convenient method of determination of f consists in the analysis of fusion curves.

The thermodynamic description of the complex formation process usually involves the calculation of $\Delta H°$, $\Delta S°$, β, and S.

Within the framework of the two-state model, the enthalpy of reaction can be determined as follows.

1. From the temperature variation of the equilibrium constant (by the van't Hoff method):

$$\ln K = -\Delta H°/RT + \Delta S°/R \ .$$

2. From the concentration variation of T_m[15,19]:

$$1/T'_{пл} = 1/T''_{пл} + R/\Delta H° \cdot \ln c'/c'' \ .$$

We may note that this method is applicable only to the description of intermolecular interaction, because intramolecular complex formation is independent of concentration.

3. From the slope of the melting curve at the point corresponding to T_m (Podder[21]):

$$(\partial f/\partial T)_m = \Delta H°/6RT_m^2 \ .$$

If the melting curve is expressed in a differential form, the formula relating the enthalpy of reaction to the half-width of the transition (T_1–T_2) can be written as follows[38]:

$$\Delta H° = -5.106 R T_1 T_2/(T_2 - T_1),$$

where T_1 and T_2 are the temperatures (K) at which $(\partial f/\partial T^{-1}) = 0.5(\partial f/\partial T^{-1})_{max}$. The enthalpy of complex formation determined by the second method agrees well with $\Delta H°$ obtained by direct calorimetric measurements [this has been demonstrated for the duplexes $d(G-C)_3$[39] (Table 1, system 9) and A_7U_7[40]].

The determination of the heat of formation of oligomeric duplexes with different numbers of base pairs makes it possible to estimate the enthalpy change per nucleotide pair[15]:

$$\Delta H° = \Delta H°_{\beta S} + (N-1)\Delta H°_S \ ,$$

where the indices βS and S denote respectively the thermodynamic parameters of the formation of the first and subsequent nucleotide pairs. If it is assumed that the stability of the oligomeric duplex is proportional to the number of monomeric units, then $\Delta H° = N\Delta H°_1$ and $\Delta S° = N\Delta S°_1$, where $\Delta H°_1$ and $\Delta S°_1$ are the thermodynamic parameters of the formation of the nucleotide pair on the assumption that all the base pairs are identical[19].

Since T_m for the duplex is usually measured more accurately than $\Delta H°$ and $\Delta S°$, it is useful to examine the dependence of T_m on the length of the oligomeric duplex. The direct proportionality between $1/T_m$ and $1/N$ has been predicted[37]:

$$1/T_m = 1/T_m^\infty + R \cdot \ln(\beta c)/N\Delta H°_1 \ ,$$

where T_m^∞ is the melting point of the corresponding polymeric complex and c the concentration of the oligomeric components. The slope of the $1/T_m - 1/N$ straight line and the intercept on the ordinate axis make it possible to determine the nucleation parameter and T_m respectively subject to the condition that $\Delta H°_1$ is known. Here it is assumed that $\Delta H°_1$ and β are constant. In real nucleotide systems the dependence of $1/T_m$ on $1/N$ frequently deviates from linearity[13,15], which indicates a temperature variation of β. If this is true, the enthalpies of the initiation ($\Delta H°_{\beta S}$) and propagation ($\Delta H°_S$) of the helix should differ. The temperature dependence of β is taken into account by introducing the stacking factor χ, which determines the relative contribution of the interplanar interactions to the enthalpy of propagation of the double helix[41]: $\Delta H°_\beta = -\chi\Delta H°_S$. The modified equation of Applequist and Damle has the following form[1]:

$$1/T_m = 1/T_m^\infty + 1/N - \chi R \ln(\beta S^\chi c)/\Delta H°_\beta \ .$$

The equation includes two limiting cases: the enthalpy of initiation is equal to the enthalpy of propagation of the helix ($\chi = 0$) and the enthalpy of initiation is zero ($\chi = 1$). The

best agreement with experimental data for the complexes oligo(A).oligo(U) is obtained when $\chi = 0.7$,[11] for $d(pG-C)_n$[15] and the hybrid complexes $d(pT)_8.rA(pA)_7$[13] when $\chi = 1$, and for the oligo(A) double helices in an acid medium when $\chi = 0$.[41]

The two-state model constitutes a good approximation for the calculation of the thermodynamic parameters of the complex formation by short oligomers. However, in each specific case it is useful to estimate the validity of the applicability of this model. The conditions governing the validity of the two-state model have been described in a review[1].

3. The Model Taking into Account the Set of States (the "Staggered Zipper Model")

In the calculation of the thermodynamic parameters of the complex formation by fairly long oligomers ($N \cong L$), it is no longer permissible to neglect the concentration of the oligonucleotides where not all the bases are linked in the complex. In order to describe the thermodynamics of such systems, Applequist and Damle[37] proposed a model taking into account the set of partially bound structures. Taking into account the equilibrium constants for each state βS^z (z is the number of paired bases), it is possible to derive the overall equilibrium constant of the complex formation reaction:

$$K_z = \beta\chi(z, N)S^z \ ,$$

where $\chi(z,N)$ is the number of possible states of the complex with z nucleotide pairs. The proposed model makes it possible to estimate quantitatively the populations of different states (for further details of the theory, see Applequist and Damle[37]). The formation of the oligo(A) double helix in an acid medium[41] as well as the complex formation by $d(A-T)_n$[16], oligo(A) + oligo(U)[11], and a large set of heterogeneous oligoribonucleotides[22] have been described thermodynamically with the aid of this model (Table 1). For comparatively short oligomeric complexes (up to 10 monomeric units), the experimental fusion curves are described satisfactorily, as stated above, by the simpler two state model and the thermodynamic parameters of the reaction obtained with the aid of the two models are very similar[22]. Since the direct application of the "staggered zipper model" is fairly complex in the interpretation of experimental data, the "all or nothing" model is usually employed as a first approximation in the determination of thermodynamic parameters. Subsequently the results are corrected on the basis of the analysis of the populations of the intermediate states.

4. The Introduction of Corrections in the Calculation of Thermodynamic Parameters

Evidently in the temperature range corresponding to the melting of oligomeric duplexes (usually at comparatively low temperatures) there is equilibrium between the double helix complex and the single stranded components in which the interplanar interactions are only partly affected. The intrinsic secondary structure of the oligomeric strands is determined by the stacking interactions of the bases, which weaken with increase of temperature[42,43]. Thus the non-cooperative process involving the breakdown of the stacking conformations of the single-stranded components is superimposed on the helix–coil transition in the oligomeric systems. In order to compare the thermodynamic parameters of the complex formation reactions in different systems, it is necessary to eliminate the stacking interactions of the oligomers, i.e. to begin the reckoning from the fully destructured state.

The contribution to the free energy of the helix–coil transition due to the breakdown of the stacking conformations of the single-stranded oligonucleotides can be represented as follows[11,22]:

$$\Delta G^0_{\text{stacking}} = RT \ln (1 + e^{\Delta G^0_A/RT})(1 + e^{\Delta G^0_B/RT}) \ ,$$

where ΔG°_A and ΔG°_B are the free energies of the stacking interaction between neighbouring bases in the complementary oligomeric chains (A and B). It is fairly difficult to calculate ΔG°_A and ΔG°_B. For this purpose, it is necessary to examine the transition of each interacting oligomer from the ordered to the disordered state and to calculate the enthalpy and entropy of this process. A simpler approach involves the use of the thermodynamic parameters of the stacking interaction of dinucleotide phosphates[13,22] This type of correction of thermodynamic data has been made for a series of oligoribonucleotide systems[11,13,22] (Table 1). It follows from the tabulated data that the enthalpies and entropies of complex formation of oligoribonucleotides calculated with and without allowance for the breakdown of the stacking conformations of the single-stranded components differ appreciably. This shows that at the melting point of the complex the intrinsic secondary structure of the oligoribonucleotide chains is only slightly affected. Since the thermal stability of the stacking conformations in oligodeoxyribonucleotides is much lower than in oligoribonucleotides[44,45], the corresponding energy contribution is not significant in the calculation of the thermodynamic parameters of the complex formation by the DNA oligomers[15]. It is of interest to note that the fraction of the stacking conformations of the single-stranded components diminishes after the addition of up to 10% of alcohols, urea, etc. to aqueous solutions[46].

The statistical theory developed by Warshaw and Cantor[47] predicts that the stacking conformations of the single-stranded oligomers are the most important of the three factors which determine the difference in the behaviour of short double helices and polymer systems. The two other factors are the influence of the terminal nucleotide pairs and the effects of the neighbouring base pairs, which are characteristic of heterogeneous oligomeric duplexes.

Electrostatic interactions also influence the free energy of complex formation. Theoretical examination of the interaction of the negative charge of the phosphate groups of the complementary nucleotide chains with the counterions predicts a linear increase of T_m with increase of the logarithm of the concentration of univalent ions in polymer systems[38,48]. For oligomeric complexes, some deviation is observed from the linear relation [for example, in the oligo(rA).oligo(dT) system[13]]. The influence of the length of the chain of the oligomeric complex on the relation between T_m and $\lg I$ (I is the ionic strength of the solution) has also been noted[14,15].

The contribution of electrostatic interactions to the free energy of the helix–coil transition is usually described by the equation[11,13,48]

$$\Delta G^0_{\text{electr}} = RT(C_1 - C_2 \lg I) \ ,$$

where C_1 and C_2 are empirical constants. According to the data of Hogget and Maass[13], the constant C_2 for oligomeric complexes can be estimated from the dependence of the stability constant of the double helix on the ionic strength of the solution.

Thus the change in free energy as a result of the increase in the length of the double helix by one nucleotide pair (ΔG°_S) can be expressed as follows taking into account the stacking interactions in the single-stranded oligomers and the electrostatic interactions[11,13]:

$$\Delta G^0_S = \Delta G^0_{12} + \Delta G^0_{\text{stacking}} + \Delta G^0_{\text{electr}} \ ,$$

Table 1. Thermodynamic parameters of the complex formation by complementary oligonucleotides.

No.	Oligomeric system	Complex formation conditions	Melting temperature range or T_m, °C	β, litre mol^{-1}	S	ΔH°, kcal mol^{-1}	ΔS°, e.u.	ΔH^0_S, kcal mol^{-1}	ΔS^0_S, e.u.	Refs.
1	A(pA)$_n$+U(pU)$_n$, N=7—17	0.5 M cacodylate buffer, pH 6.9	10—35	$5\cdot10^{-4}$—10^{-3}	7.9(0°)	—	—	—10.9	—30	[11]
2	d(pT)$_7$+rA(pA)$_6$	0.1 M cacodylate buffer, pH 7.0	5—30	10^{-4}—$5\cdot10^{-4}$	21(0°)	—73.5	—218	—11.2	—30.7	[13]
	d(pT)$_8$+rA(pA)$_7$	1 M NaCl	5—30	10^{-4}—$5\cdot10^{-4}$	21(0°)	—84	—253	—11.2	—30.7	
	d(pT)$_9$+rA(pA)$_8$		5—30	10^{-4}—$5\cdot10^{-4}$	21(0°)	—90	—264	—11.2	—30.7	
3	GpGpGpC+GpCpCpC	0.1 M phosphate buffer, pH 7.2	20—40	10^{-3}	~100 (22—39°)	—21.6	—50	—6—7	—12.5	[21]
4	(Ap)$_3$ApU(pU)$_3$	0.01 M phosphate buffer, pH 7.0, 1 M NaCl, 10^{-4} M EDTA; $c = 10^{-4}$ M	12	$1.4\cdot10^{-4}$	—	—54(—46)	—	—6.4(—5.8)	—19.8	[19]
	(Ap)$_4$ApU(pU)$_4$		23	$1.4\cdot10^{-4}$	—	—72(—53)	—	—7.2(—5.3)	—19.8	
	(Ap)$_5$ApU(pU)$_5$		32	$1.4\cdot10^{-4}$	—	—85(—56)	—	—7.1(—4.8)	—19.8	
	(Ap)$_6$ApU(pU)$_6$		40	$1.4\cdot10^{-4}$	—	—107(—72)	—	—7.6(—5.1)	—19.8	
5	(Ap)$_3$CpG(pU)$_3$	0.01 M phosphate buffer, pH 7.0, 1 M NaCl, 10^{-4} M EDTA; $c = 10^{-4}$ M	35.3	$2.2\cdot10^{-4}$	—	—65	—	—7.6	—	[49]
	(Ap)$_4$CpG(pU)$_4$		42.5	$2.2\cdot10^{-4}$	—	—76	—	—7.6	—	
	N=6									
	A$_4$CG+CGU$_4$	0.01 M phosphate buffer, pH 7.0, 1 M NaCl, 10^{-4} M EDTA; $c = 10^{-4}$ M ($A+A$ helix) and 2×10^{-4} ($A+B$ helix)	~1.3	—	—	—26	—75.8	see Table 2	see Table 2	[23]
	U$_2$CA$_2$		11.3	—	—	—37	—112			
	A$_2$CU$_2$		22.1	—	—	—34	—96.9			
	A$_4$G$_2$+C$_2$U$_4$		22.8	—	—	—44	—129			
	A$_2$CGU$_2$		28.3	—	—	—46	—134			
	N=7									
6	A$_3$CU$_3$+A$_3$GU$_5$	ditto	16.4	—	—	—41	—122	ditto	ditto	[23]
	N=8									
	A$_8$U$_8$	»	11.5	—	—	—51	—160	»	»	[23]
	A$_4$CU$_3$+A$_3$GU$_4$		22.1	—	—	—52	—156	»	»	
	A$_3$CGU$_3$		35.1	—	—	—66	—196			
	A$_3$GCU$_3$		42.3	—	—	—53	—150			
	N=9									
	A$_4$CU$_4$+A$_4$GU$_4$	»	26.0	—	—	—58	—174	»	»	[23]
	N=10									
	A$_5$U$_5$	»	24.3	—	—	—67	—207	»	»	[23]
	A$_4$UAU$_4$		27.7	—	—	—72	—221			
	A$_5$CU$_4$+A$_4$GU$_5$	»	32.6	—	—	—63	—187			
	A$_4$CGU$_4$		41.9	—	—	—76	—223			
	A$_4$GCU$_4$		46.8	—	—	—78	—225			
	N=11									
	A$_5$CU$_5$+A$_5$GU$_5$	»	35.4	—	—	—89	—269	»	»	[23]
	N=12									
	A$_6$U$_6$	»	31.5	—	—	—84	—257	»	»	[23]
	N=14									
	A$_7$U$_7$	»	39.3	—	—	—107	—324	»	»	[23]
7**	A$_2$GCU$_2$	0.05 M cacodylate buffer, pH 7.0; $c = 10^{-5}$ M ($A+A$) and 2×10^{-5} M ($A+B$)	8	$5\cdot10^{-4}$	170	—72	—215	(—14)—15	—38.0	[22]
	A$_3$GCU$_3$		20	$5\cdot10^{-4}$	200 } 170	—92	—268	(—12)—15	—36.8	
	A$_4$GCU$_4$		25	$5\cdot10^{-4}$	140	—111	—326	(—12)—15	—37.7	
	A$_6$CG+CGU$_6$		7	10^{-3}	67 } 60	—95	—289	(—15)—15	—41.2	
	A$_8$CG+CGU$_8$		16	10^{-3}	53	—102	—304	(— 9)—14	—38.0	
	A$_4$G$_2$+C$_2$U$_4$		1	10^{-3}	110 } 130	—76	—233	(—16)—15	—39.5	
	A$_5$G$_2$+C$_2$U$_5$		6	10^{-3}	150	—87	—265	(—16)—17	—47.1	
	A$_4$G$_3$+C$_3$U$_4$		22	10^{-3}	108 } 95	—76	—216	(—11)—11	—25.2	
	A$_5$G$_3$+C$_3$U$_5$		24	10^{-3}	86	—88	—254	(—11)—11	—27.3	
8*	GpApGpC+GpCpUpC	0.01 M phosphate buffer, pH 7.0, 0.1 M NaCl, 10^{-4} M EDTA; $c = 10^{-4}$ M ($A+A$) and 2×10^{-4} M ($A+B$)	17.7	—	—	—24.4(—39.1)	—	—	—	[50]
	GpApGpC+ApGpCpUpC		16.0	—	—	—24.4(—30.7)	—	—	—	
	ApGpCpU pC		6.0	—	—	—29.3(—25.9)	—	—	—	
9	oligo d(pG—C) N=4—7	0.045 M phosphate buffer, pH 7.2, 1 M NaCl, 2×10^{-3} EDTA	10—70	$1.6\cdot10^{-4}$	104±5 (25°)	—28.8 (N=4) —38.5 (N=5) —50.7 (N=6) —60.2 (N=7)	—	—11.1±0.5	—27.9±1	[15]
	d(G—C)$_3$*	0.045 M cacodylate buffer, pH 7.0, 1 M NaCl; $c = 2.9\times10^{-5}$ M	50	—	—	—56.9(—59.6)	—	—	—	[39]
	d(G—C)$_3$*	0.045 M cacodylate buffer, pD 7.3, 1 M NaCl (D_2O)	—	—	—	—62.7(—65.8)	—	—	—	[39]
10	d(A—T—G—C—A—T)	cacodylate buffer, pD 7.0 (D_2O)	20—40	—	—	—34	—	—	—	[51]
11	d(T—T—G—T—T)+ +d(A—A—C—A—A)	0.1 M phosphate buffer, pD 7.0, 0.15 M NaCl (D_2O)	0—30	—	—	—34	—	—	—	[24]
12	d(G—G—A—A—T—T—C—C)	0.01 M phosphate buffer, pH 6.85, 10^{-3} M EDTA, 0.1 M NaCl; $c = 5.3\times10^{-3}$ M	46±3	—	—	—51.8	—151	—	—	[52]
13	dC(pA)$_5$pG+dC(pT)$_5$pG	0.01 M phosphate buffer, pH 7, 10^{-4} M EDTA, 0.2 M NaCl; $c = 2\times10^{-4}$ M	27.5	—	—	—41±4	—	—	—	[53]
	rC(pA)$_5$pG+dC(pT)$_5$pG		22.9	—	—	—48.4	—	—	—	
	rC(pA)$_5$pG+rC(pU)$_5$pG		19.1	—	—	—44±4	—	—	—	
	dC(pA)$_5$pG+rC(pU)$_5$pG		<0	—	—	—	—	—	—	
14***	d(pA—C—C)$_2$+ +d(pG—G—T)	0.004 M phosphate buffer, pH 7.3, 0.2 M NaCl, 0.075 M $MgCl_2$; $c = 0.8\times10^{-2}$ M	11(9)	$0.5\cdot10^{-3}$	35(10°)	—65 (—54)	—197 (—163)	—10.4	—30.6	[18]
	d(pA—C—C)$_3$+ +d(pG—G—T)		18(18)	$0.5\cdot10^{-3}$	20(16°)	—98 (—87)	—288 (—262)	—10.4	—30.6	
	d(pA—C—C)$_4$+ +d(pG—G—T)		22(23)	$0.5\cdot10^{-3}$	19(23°)	—122(—119)	—355 (—343)	—10.4	—30.6	
	d(pA—C—C)$_2$+ +d(pT—G—G)		9(9)	$0.5\cdot10^{-3}$	—	—(—47)	— (—138)	—10.4	—30.6	
	d(pA—C—C)$_3$+ +d(pT—G—G)		18(18)	$0.5\cdot10^{-3}$	32(16°)	—(—78)	— (—226)	—10.4	—30.6	
	d(pA—C—C)$_4$+ +d(pT—G—G)		21(22)	$0.5\cdot10^{-3}$	23(22°)	—(—106)	— (302)	—10.4	—30.6	
	d(pC—C—A)$_2$+ +d(pG—G—T)		9(9)	$0.5\cdot10^{-3}$	59(9°)	—64 (—58)	—198 (—176)	—10.4	—30.6	

Table 1 (Cont'd.)

No.	Oligomeric system	Complex formation conditions	Melting temperature range or T_m, °C	β, litre mol^{-1}	S	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, e.u.	$\Delta H°_S$, kcal mol^{-1}	$\Delta S°_S$, e.u.	Refs.
	d(pG—C—A)$_2$+ +d(pT—G—G)		8(9)	$0.5\cdot10^{-3}$	—	—(—60)	—(—183)	—10.4	—30.6	
	d(pT—G—G)$_2$+ +d(pC—C—A)		3(2)	$0.5\cdot10^{-3}$	—	—(—65)	—(—204)	—10.4	—30.6	
	d(pA—C—C)$_2$+ +d(pT—G—G)$_2$		13(15)	$0.5\cdot10^{-3}$	—	—(—53)	—(—169)	—10.4	—30.6	
15***	d(T—G—C—A—C—A—T—G)	0.004 M phosphate buffer, pH 7.3, 0.2 M NaCl, 0.075 M $MgCl_2$; $c = 10^{-3}$ M	20	—	—	—74.0±2.4	—216±8	—9.2±0.3	—27±1	[29]

Note. The thermodynamic parameters of systems 1, 2, and 8 were calculated taking into account the breakdown of the stacking conformation of the single-stranded components. The two-state model (systems 2–6 and 8–15), the model taking into account the set of states (system 1), or both models (system 7) were used in the calculation (the values of $\Delta H°_S$ calculated on the basis of the two-state model are given in brackets); the abbreviations for the oligonucleotides were taken from the original communications.

* The values of $\Delta H°$ and $\Delta H°_S$ calculated in different ways are quoted.

** The values of $S°$, $\Delta H°_S$, and $\Delta S°_S$ refer to the formation of the G:C pairs.

*** The values of T_m, $\Delta H°$, and $\Delta S°$ calculated from the temperature variation of the CD parameters are quoted; the values evaluated from the temperature variation of the ultraviolet absorption are given in brackets.

**** The values of $\Delta H°$ and $\Delta S°$ for $n = 3$ (n is the number of octanucleotide molecules involved in the formation of the concatamer) are quoted.

where $\Delta G°_{12}$ is the energy of formation of the additional nucleotide pair from the statistical coil with uncharged phosphate groups.

The chain propagation constant $S = e^{\Delta G°_S/RT}$. The breakdown of the stacking conformations of the single-stranded oligomers and electrostatic interactions also influence the initiation of the double helix[11].

The thermodynamic parameters of the formation of oligomeric complexes of different composition and length, calculated resorting to different models, are summarised in Table 1. The first detailed thermodynamic studies of the complex formation by oligoribonucleotides were undertaken by Pörschke[11] [oligo(A).oligo(U)] and in the studies of Martin et al.[19] and Uhlenbeck et al.[49] [$(Ap)_nApU(pU)_n$ and $(Ap)_nCpG(pU)_n$]. Subsequently oligomeric duplexes with a greater variety of compositions and nucleotide sequences were investigated. The thermodynamic parameters of 19 RNA duplexes containing between 6 and 14 nucleotide pairs have been reported[23]. The thermodynamics of the formation of DNA duplexes have also been investigated: self-complementary oligomers with the repeating dinucleotide sequences $d(A-T)_n$[16] and $d(pG-C)_n$[15], with the heterogeneous sequences d(A—T—G—C—A—T)[51], d(G—G—A—A—T—T—C—C)[52], etc. (Table 1). A thermodynamic description of the formation of double helical oligodeoxyribonucleotide complexes with breaks in the chain of phosphodiester bonds, including complexes of the concatameric type, has been achieved recently[18,29,30].

IV. CHARACTERISTIC FEATURES OF THE THERMODYNAMICS OF COMPLEX FORMATION BY HETEROGENEOUS OLIGONUCLEOTIDES

1. The Stability of the A:U(T) and G:C Pairs

The increase of the thermal stability of natural DNA and synthetic double helix polynucleotides with increase of the relative content of the G:C pairs is a well known experimental fact[54]. The correlation between the content of the G:C pairs and the stability of the helices has been demonstrated also at the level of oligomeric complexes. Thus, in a study[49] on the stability of the complexes of the block copolymers $(Ap)_nApU(pU)_n$, $(Ap)_nCpG(pU)_n$, and $(Ap)_nG(pU_n)(Ap)_n\cdot C(pU)_n$, it was shown that T_m of the double helices increases in direct proportion to the percentage content of the G:C pairs; with increase of the content of such pairs by 1%, T_m of the complexes increases on average by 0.9°. For natural DNA and RNA, the corresponding increments are 0.5° and 0.75° respectively. The enhanced stability of the G:C pairs in the oligomeric duplexes is believed[49] to be caused by the fact that the nucleotide sequence of the base pairs in the duplexes is far from the quasi-statistical distribution characteristic of the natural nucleic acids. The enthalpy of complex formation by $(Ap)_nCpG(pU)_n$ is significantly higher than the enthalpy of complex formation by $(Ap)_nApU(pU)_n$: −65 and −54 kcal mol^{-1} respectively (for $N = 8$). According to the authors' estimate[49], $\Delta H°_{G:C}$ is higher by ~ 3–4 kcal mol^{-1} than $\Delta H°_{A:U}$.

The study of duplexes containing complementary pairs of one type permitted the calculation of the thermodynamic parameters of the formation of the A:U(T) or G:C pairs. The value of $\Delta H°_{G:C}$ obtained from the study of the complex formation by $d(pG:C)_n$[15], which is −11.1 kcal mol^{-1}, greatly exceeds $\Delta H°_{A:U}$, which has been estimated as −8 kcal mol^{-1},[16] while the free energy of a single G:C pair at 37 °C corresponds to the free energy of two A:T pairs. Fig.2 presents the dependence of the thermodynamic parameters of the formation of nucleotide pairs on the composition of the deoxyribonucleotide duplexes.

The enthalpies of formation of the G:C and A:U pairs obtained with and without allowance for the stacking interactions in the oligomers have been compared[22]. In a study of the complex formation by a large set of oligoribonucleotide with a heterogeneous composition, it was established[22] that the enthalpy of formation of the G:C pair from a fully destructured coil (−15 kcal mol^{-1}) is higher than the corresponding value for the A:U pair (−10.7 kcal mol^{-1}). If a correction taking into account the temperature dependence of the stacking conformation of the single-stranded oligomers

is applied in the calculation of the enthalpy, then the difference between $\Delta H^{\circ}_{G:C}$ (−5 − −6 kcal mol^{-1}) and $\Delta H^{\circ}_{A:U}$ (−5 − −6 kcal mol^{-1}) virtually disappears, because the two bases in the G:C pairs interact with the neighbouring bases, whereas the stacking interactions in the A:U pair with participation of uracil are insignificant.

The stability constants S of the G:C and A:U(T) pairs have been calculated for a series of ribo- and deoxy-ribonucleotide complexes (Table 1). Comparison of $S_{G:C}$ (100–200) with $S_{A:U}$ (~ 10) shows that the G:C pair is on average 15 times more stable than the A:U(T) pair.

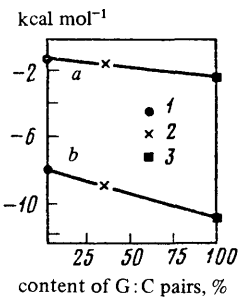


Figure 2. ΔG°_{S} (*a*) and ΔH°_{S} (*b*) for the formation of nucleotide pairs in DNA of different composition at 37 °C (1 M NaCl, pH 7.0): 1) poly d(A–T); 2) T-2:phage DNA; 3) oligo [d(pG–C)].[15]

2. The Influence of the Nucleotide Sequence and Other Factors on the Stability of the Duplexes

It follows from the analysis of the data in Table 1 (system 7) that $S_{G:C}$ depends on the nucleotide sequence of the oligomeric components, i.e. the stability of the oligomeric complexes is influenced not only by the length of the helix and the nucleotide composition but also by the sequence of the base pairs in the chain (nucleotide environment). The dependence of the thermal stability of nucleotide complexes on the base pair sequence was observed for the first time for synthetic polymer systems with a repeating di(tri)nucleotide sequence[55,56].

According to modern ideas[23], the difference between the stabilities of the isomeric complexes is due to the different geometries of the "stacking" of neighbouring base pairs in the helical structures. Theoretical calculations predict that the contribution of each base pair to the stability of the complex depends mainly on the nearest neighbouring base pairs, although in real systems it is frequently impossible to neglect the contribution of long-range interactions. Evidently the influence of the nucleotide sequence should be manifested most strikingly in the properties of short oligomeric complexes. Indeed, when five isomeric helices containing two G:C and four A:U pairs are compared, the T_m of these complexes under the conditions of identical nucleotide concentrations vary from −1.3° to 28.3 °C.[23] An increase in the length of the nucleotide chain leads to a gradual averaging of the thermodynamic parameters and in the limit this effect is not manifested for polymeric structures with a statistical distribution of bases along the chain.

By considering only the Watson–Crick A:U(T) and G:C interactions, it is possible to formulate 10 different combinations of two nucleotide pairs, i.e. 10 different ways in which the interplanar interactions between two base pairs in the double helix can take place:

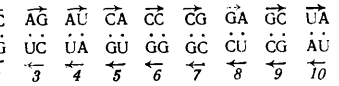
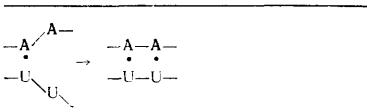
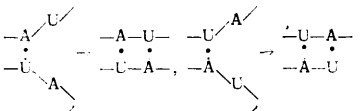
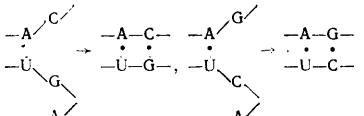
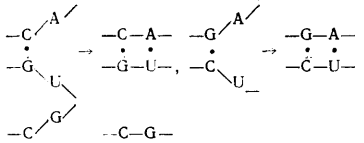
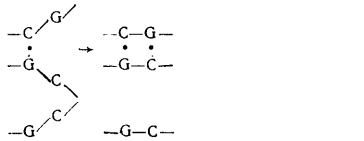
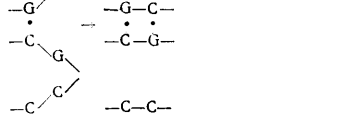


Table 2. Thermodynamic parameters of the formation of the nucleotide pair next to a base pair already formed (for all possible combinations of two Watson–Crick pairs)*[23].

Reaction	ΔH°_{S}, kcal mol^{-1}	ΔS°_{S}, e.u.	ΔG°_{S}, kcal mol^{-1} 25 °C
	−8.2	−23.5	−1.2
	−6.5	−16.4	−1.6
	−5.9	−12.7	−2.1
	−13.0	−33.5	−3.0
	−14.7	−34.9	−4.3
	−13.7	−29.8	−4.8

* The calculation was based on the thermodynamic data presented in Table 1 for these systems[23].

Gralla and Crothers[57] isolated three combinations of two pairs of bases—two neighbouring A:U pairs in any order, two neighbouring G:C pairs in any order, and two neighbouring A:U and G:C pairs in any order, and obtained three equilibrium constants for the description of the helix–coil equilibrium on the basis of the interaction of the neighbouring pairs. The study of the thermodynamics of the series of oligomeric duplexes of different compositions and with different nucleotide sequences permitted[23] the calculation of the thermodynamic contributions of six combinations of nucleotide

pairs. Table 2 presents the ΔH_S°, ΔS_S°, and ΔG_S° for the formation of a specific nucleotide pair next to one already formed. It is seen from the tabulated data that the $\begin{matrix}\rightarrow\\ CC\\ \cdot\cdot\\ GG\\ \leftarrow\end{matrix}$ doublet is more stable than $\begin{matrix}\rightarrow\\ GC\\ \cdot\cdot\\ CG\\ \leftarrow\end{matrix}$, which is in its turn more stable than $\begin{matrix}\rightarrow\\ CG\\ \cdot\cdot\\ GC\\ \leftarrow\end{matrix}$, while the complex consisting of a block of G:C pairs followed by a block of A:U pairs is more stable than the double helix containing repeating A:U and G:C pairs. We may note that it has recently been possible to determine the equilibrium constants for the dimerisation of dideoxyribonucleotides with different sequences by NMR[58]. The sequence of the stabilities of the corresponding minihelices is fully consistent with that predicted by Borer et al.[23]: d(pG–G).d(pC–C) ≥ d(pG–C).d(pG–C) > d(pC–G).d(pC–G). The stabilities of short double helix complexes can be predicted fairly accurately with the aid of the calculated thermodynamic chain propagation parameters and the T_m of polymeric structures with known sequences can be estimated approximately).

It has been observed[59] that the T_m of the double-stranded tetranucleotides C–A–U–G, U–G–C–A, and A–G–C–U, containing equal numbers of the G:C and A:U pairs, are different (25°, 33°, and 34° respectively), i.e. the duplexes with A:U pairs at the ends are more stable than those which terminate in G:C pairs. It has been suggested[59] that a central core of G:C pairs leads to an increase of stability.

One of the factors which increase the stability of the duplexes is the flanking of the double helix by an unpaired (looped) nucleotide residue[19,59], purine nucleotides leading to a greater stabilisation (by ~ 11°) than pyrimidine nucleotides (by ~ 5°).[59] The location of the additional nucleotide residues (the 3′- or 5′-end) is not very important[59]. The cause of the increased stability of the duplex is not completely clear. One of the explanations[6] consists in the fact that the additional "stacking" with the looped bases stabilises the terminal pairs of the duplex, which would otherwise frequently become uncoupled at temperatures below T_m (see below). If the length of the non-complementary shoulders amounts to several nucleotide residues, then the stability of the oligomeric duplexes actually diminishes. For example, a mixture of two icosanucleotides, capable of forming 10 nucleotide pairs, altogether fails to exhibit a cooperative melting profile[60].

Comparison of the stabilities of a series of seven-unit duplexes (system 13, Table 1) of the deoxyribo-series, the ribo-series, and hybrids with similar compositions and sequences (in oligoribonucleotides T is replaced by U) showed that the duplex $dC(pA)_5pG.rC(pU)_5pG$ with the oligo(dA.rU) sequence is extremely unstable, in contrast to the remaining duplexes[3]. The dA clusters with a length corresponding to ~ 5 pairs apparently assume preferentially the B-DNA conformation as a result of which they cannot form stable DNA–RNA hybrids. According to Martin and Tinoco[53], this facilitates the termination of transcription. The influence of the solvent on the thermodynamics of the $d(G–C)_3$ complex formation has been examined[46]. The addition of primary alcohols, formamide, dimethylformamide, or urea to an aqueous buffer solution of $d(G–C)_3$ destabilises the double helix.

V. KINETICS OF THE FORMATION AND DISSOCIATION OF THE OLIGOMERIC COMPLEXES

The kinetic parameters of the formation or dissociation of nucleotide complexes are usually obtained with the aid of the temperature jump method, which is based on the measurement of the time variation of various physicochemical parameters of the system, for example, ultraviolet absorption, after an abrupt increase of temperature. One then obtains the so-called relaxation curve. A characteristic feature of these curves is the relaxation time τ. In all the intermolecular oligomeric complexes investigated the reaction involving the formation of the complementary pairs is of second order and is characterised by a unique relaxation time (from 10^{-3} to 1 s)[22,61] and the temperature at which the maximum amplitude of the relaxation curve is attained is close to the T_m of the duplex[21].

The relaxation time, characterising the complex formation reaction of the oligomers, is related directly to the rate constants for the formation (k_r) and dissociation (k_d) of the double helix and the equilibrium concentrations of the complementary chains (c_A and c_B)[13,22]:

$1/\tau = 4k_r c_A + k_d$ (complex formation by self-complementary oligonucleotides: $A \underset{k_d}{\overset{k_r}{\rightleftharpoons}} AA$);

$1/\tau = k_r(c_A + c_B) + k_d$ (complex formation by non-identical oligomers: $A + B \underset{k_d}{\overset{k_r}{\rightleftharpoons}} AB$).

The rate constants for the forward and reverse reactions can be estimated by plotting $1/\tau$ against the concentration of the free chains.

The complex formation by oligonucleotides can be regarded as a process involving the successive formation of complementary pairs. Since the formation of the nuclei of a nucleotide pair (or several pairs) is a second-order reaction, this stage is a more complex and slower process than the subsequent growth of the double helix[62]. If the formation of the first nucleotide pair is the rate-limiting stage in the complex formation process, then the enthalpy of activation for the latter (ΔH_r^*) should be identical with that of the elementary reaction whose rate is limited by the diffusion of the components: +2 – 6 kcal mol^{-1}.[22] However, the ΔH_r^* for oligo(A) in an acid medium[41], for oligo(A).oligo(U)[61], and oligo(rA).oligo(dT)[13] are negative. In order to resolve this contradiction, Eigen and Pörschke[41] suggested that the stage limiting the rate of the recombination process is the formation of a stable core made up of several nucleotide pairs. The formation of a stable nucleus of the helix is preceded by a stage involving pre-equilibrium between the rapidly formed and decomposed unstable nucleotide pairs. Further growth of the double helix is very rapid. The overall recombination rate constant is then independent of the length of the oligomer chain[13]. On the basis of the analysis of the ΔH_r^*, it was established that, for the complexes containing only the A:U(T) pairs, the core of the helix incorporates ~ 3 pairs of bases[13,41,61,62].

Since the association constant of the G:C pairs is ~ 15 times greater than for the A:U(T) pairs, the recombination of oligonucleotides of mixed composition begins with the formation of the G:C pairs[22]. In these systems k_r changes from 10^5 to 10^7 litre mol^{-1} s^{-1}.[21,22,25,51]. For the $(A)_n.(U)_n.[(T)_n]$ helices, k_r is of the same order of magnitude (10^6 litre mol^{-1} s^{-1}).[61] Having investigated the kinetics of complex formation in heterogeneous systems, Pörschke et al.[22] isolated three characteristic kinetic features: (1) in the given series of oligomers the rate of recombination diminishes rapidly with increase of chain length; (2) the rate of recombination diminishes rapidly with increase of chain length; (2) the rate of recombination of oligomers with identical chain lengths is 6 times faster when the G:C pairs are at the end of the helix and not in its centre; (3) the enthalpy of activation for the formation of oligomeric duplexes containing G:C pairs is positive.

According to the authors[22], the first two features can be explained by the different accessibility of the G:C pairs initiating recombination in oligomeric systems with different nucleotide sequences and lengths. The positive enthalpy of activation for the complex formation by heterogeneous oligomers[21,22] is associated with the fact that the rate-limiting stage in the recombination process is the formation of one or possibly two G:C pairs. In this case there is no need to employ a model incorporating a stage with pre-equilibrium between several pairs of bases.

The dissociation of oligomeric duplexes is much slower than their formation[21,22,25,51,61]. In contrast to k_r, the rate constant for the dissociation of the duplex depends greatly on the length of the helix, i.e. on the number of nucleotide pairs which must be ruptured before the critical intermediate helix is attained[13,22]. The activation enthalpy for the dissociation process ΔH_d^* increases with increasing chain length[13,62].

VI. COMPLEMENTATION INTERACTIONS OF DINUCLEOTIDES

A characteristic property of double helical oligonucleotides is the dependence of the stability of the complex on the chain length and the nucleotide concentration. The relation between T_m, N, and c is given by the equation of Applequist and Damle (see above). The shorter the oligomers, the higher must be their concentration in order to observe the formation of the complementary complex. Thus, at an overall nucleotide concentration of 10^{-4} M, the oligomers capable of complementation interactions must comprise at least several mononucleotide units[10,14]. An increase of nucleotide concentration by a factor of 10 promotes the formation of complexes of tetramers[10]. In connection with the development of the high-resolution NMR technique, in recent years it has proved possible to observe in an aqueous medium the interactions between complementary dinucleotides constituting the smallest structural units containing the 3′ → 5′ phosphodiester linkages. It has been shown[58,63,64] that, in aqueous solutions at high nucleotide concentrations (up to 0.1 M), the self-complementary dinucleoside monophosphates of the ribo-series, namely CpG and GpC[63], and their deoxyanalogues[58], as well as the dinucleotides d(pC–G) and d(pG–C)[58,64] form hydrogen bond–stabilised dimers at low temperatures. The formation of complementary pairs was also observed in concentrated solutions of the CpU + ApC,[53] d(pG–G) + d(pC–C), and d(pG–T) + d(pA–C)[58] mixtures. It is noteworthy that, even at the level of dinucleotide complexes, the dependence of the thermal stability of the miniature double helices on the content of G:C pairs is manifested. Thus a less stable complex is formed in the GpU + ApC mixture than the complex arising in concentrated GpC (CpG) solutions as a result of the self association of the dinucleoside monophosphates, while in the UpA solution and also in the crystalline state (see below) complex formation is not observed at all[63].

VII. THE STRUCTURE OF THE OLIGOMERIC COMPLEXES

1. X-Ray Diffraction Analysis

The most exhaustive information about the steric structure of the double helix oligonucleotides can be obtained by their crystallographic investigation. Single crystals of the following self-complementary oligonucleotides have now been investigated by high-resolution (< 2 Å) X-ray diffraction analysis, which makes it possible to trace individual atoms: UpA[65,66], ApU[67], GpC[68,69], d(pA–T–A–T)[70], and d(C–G–C–G–C–G)[71]. The d(C–G–C–G)[72,73], d(C–G–C–G–A–A–T–T–C–G–C–G)[74,75], and d(G–G–T–A–T–A–C–C)[76] single crystals have been studied with a somewhat smaller resolution (2.25–2.7 Å). In addition, the X-ray diffraction patterns of yet another dimer, namely TpdA, were obtained in 1976.[77] However, instead of single crystals, "oriented" specimens of TpdA, in which the TpdA molecules were built into helical structures (the limit of the resolution in the X-ray diffraction of fibres usually does not exceed 3–4 Å), were investigated.

Among the self-complementary dimers enumerated, only ApU and GpC form Watson–Crick pairs in the crystalline state. The crystal structure of UpA models the loop-like sections of RNA as a result of the specific conformation of the phosphodiester linkage, while TpdA forms unique left-handed helical structures in which the adenine and thymine residues of neighbouring molecules are linked by hydrogen bonds in the "Hoogsteen" manner. We shall dwell in greater detail on the description by Rich and coworkers[67,69] of the crystal structures of ApU and GpC, because theirs were the first data on the Watson–Crick pairs with atomic resolution. Two ApU (or GpC) molecules form in the crystal a segment of the right-handed RNA double helix with the antiparallel directions of their chains. The complementary bases do not lie precisely in a single plane but are slightly tilted. In each chain the bases are arranged in a stack, overlapping to the maximum extent. Such complete "stacking" is a consequence of the purine–pyrimidine sequence of dinucleoside phosphates. The distance between the C(1′) atom of the ribose residues in the A:U pairs is somewhat shorter than the analogous distance in the G:C pairs. This means that the double-helical skeleton is not a completely regular structure but one with systematic "variations", which depend on the nature of the bases. Finally the sites where the counterions are bound depend on the composition and sequence of the bases. The binding of Na^+ ions alters the steric and electrostatic characteristics of the double helix in the sections containing the ApU sequence.

d(pA–T–A–T)[70] in the crystalline state forms a segment of a right-handed double helix with the antiparallel directions of the chains and two pairs of bases stabilised by hydrogen bonds between the first A and the second T in one molecule and the fourth T and the third A in another. The mononucleotide units not involved in the complementation interaction are remote from one another in space. A characteristic feature of the steric structure of d(pA–T–A–T) is different conformations of deoxyribose [C(3′)-*endo* for A and C(2′)-*endo* for T] and different angles of rotation about the glycosidic linkages for the thymidine and adenine residues. The conformations of the phosphodiester linkage in the ...ApT... and ...TpA... fragments also differ. These data served as the starting point for the description of the unusual conformation and hence the special biological role of the poly[d(A–T)].poly[d(A–T)] sections of DNA. Klug et al.[78] suggested that in solution poly[d(A–T)].poly[d(A–T)] assumes the so-called alternating *B* form. In contrast to the classical *B* form of DNA, the repeating structural motif in this double helix consists of two nucleotide pairs.

The most striking results, leading to the discovery of the left-handed double helix of DNA, were obtained by Rich's group in an X-ray diffraction study of d(C–G–C–G–C–G) crystals (resolution 0.9 Å; crystallisation under the conditions of a high ionic strength)[71]. The repeating structural element in this helix, containing 12 G:C pairs per turn, consists of two nucleotide pairs. The alternating guanosine and cytidine residues have different conformations of the glycosidic linkage and of the furanose ring: *syn*- and C(3′)-*endo* for G and *anti*- and C(2′)-*endo* for C. The configuration of

the carbon–phosphate skeleton is very unusual: the phosphate groups are arranged in a zig-zag. This led the authors[71] to call the new structure the *Z*-DNA. Soon the left-handed *Z*-form was discovered also in d(C–G–C–G) on crystallisation at a high ionic strength)[72] and in the poly[d(G–C)].poly[d(G–C)] fibres[79,80]. In their study of the conformational variability of d(C–G–C–G) in the crystalline state, Drew and Dickerson[73] concluded that the *Z*-DNA has a greater conformational flexibility than the *B* form. They described the structural transition from *Z* to *Z'*, associated with a change in the conformation of the furanose ring of guanosine [C(3')-*endo* → C(1')-*exo*] and also the $Z_I \rightarrow Z_{II}$ transition characterising the change in the orientation of the phosphodiester linkage in the ...GpC... unit. The authors conclude that *Z'*, Z_I, and Z_{II} are conformational variants within the limits of the *Z* form. It is of interest that the dodecamer d(C–G–C–G–A–A–T–T–C–G–C–G) exists in the crystalline state as the *B* form with 10.1 bases per turn of the helix, i.e. the terminal C–G–C–G sections are not twisted into the *Z* helix[74].

In 1981 Dickerson and Drew[75] made a detailed X-ray diffraction study with a nearly atomic resolution of the dodecanucleotide d(C–G–C–G–A–A–T–T–C–G–C–G), which forms in the crystalline state a complete coil of the double helix in the *B* form. As a result of the crystal packing effect, the axis of the helix of this duplex is somewhat bent and deviates from the vertical by 19°. It was demonstrated rigorously for the first time that the local parameters of the double helix depend on the sequence of bases, deviating from the classical *B* form, the influence of the nucleotide sequence on the structure of the duplex being much more significant than the influence of the crystal packing and other external factors. Although the local changes in the conformation of the duplex take place within the limits of the *B* form, sections of the double helix whose geometry is more characteristic of the *A* or *D* forms of DNA have been observed. It has been found that purine–pyrimidine steps open their base planes toward the major groove [of the double helix], pyrimidine–purine steps open toward the minor groove"; the bases in the complementary pairs are twisted like the propeller blades and to a greater extent in the A:T pairs. The authors[75,81] reached the important conclusion on the basis of the correlation between the degree of exposure of the sections of the carbohydrate–phosphate skeleton and the rate of cleavage of these sections by the enzyme DNase I, namely that the structure of the dodecanucleotide duplex is identical in both the crystalline state and in solution.

In the next communication of this series[82] the hydrate shell of d(C–G–C–G–A–A–T–T–C–G–C–G) in the crystal was described. It was found that 72 water molecules are arranged around each molecule of the duplex, 50 of which are within the grooves of the helix or in the first coordination shell of the phosphate groups. An attempt was made to estimate the contribution of this factor to the stability of the double helix. The electrostatic potential and the steric accessibility of the reactive sites of the self-complementary dodecamer were calculated from X-ray diffraction data[83]. It was found that a higher negative potential than at the ends is concentrated in the centre of the oligonucleotide duplex. This may be a common feature of such short helices, which is independent of their nucleotide sequence.

The possibility of a wide variety of conformations of the oligonucleotide duplexes of the deoxy-series has been demonstrated[76] in a crystallographic study of d(G–G–T–A–T–A–C–C) containing the fragment of the promoter region of the eukaryotes. It was found that this octamer forms a right-handed double helix in the *A* form. This unusual fact was observed for the first time for deoxyribonucleotide duplexes containing the G:C and A:T pairs. The existence of an oligomer with this sequence in the stable *A* form can be logically related to the functions of the promoter region.

The advances in the X-ray diffraction study of single crystals of self-complementary oligonucleotides open a new page in the study of the fine structure and conformational possibilities of nucleic acids. There is no doubt that the number of complexes investigated by this method will continuously grow, because information about the structural characteristics of nucleic acids is extremely important at the present stage for the elucidation at the molecular level of the mechanism of the protein–nucleic acid recognition and the regulation of gene activity, and mutagenesis.

2. Ultraviolet Spectroscopy and CD(ORD)

Optical methods, namely ultraviolet spectroscopy and CD(ORD), have found extensive applications in the study of the complementation interactions of oligonucleotides in solution. The stoichiometry of the bonding in oligomeric systems is determined with the aid of these methods[10,20]. The formation of a duplex is inferred from the change in the form of the CD spectra of the complementary (self-complementary) oligonucleotides[18,29,84]. Sometimes, in order to achieve more appreciable changes in CD, a ligand which interacts selectively with a double-helical structure, for example distamycin A, is added[84]. The study of the temperature variation of the ultraviolet absorption and the CD(ORD) parameters make it possible to determine T_m and to calculate the thermodynamic parameters of the formation of complementary pairs (Table 1). The change in the ultraviolet absorption of oligonucleotides during the formation (dissociation) of the double helix constitutes the basis of the determination of the kinetic characteristics of the complex formation[13,21]. Furthermore, the ultraviolet spectroscopic and CD(ORD) methods yield useful information about the secondary structure of oligomeric duplexes.

The structural aspects have been traced in a study by Pohl[85] of the dependence of the hypochromicity of the complexes formed by $d(pG–C)_n$ on the number of base pairs in the double helix. Analysis of this relation enabled the author to conclude that the geometrical parameters of the oligomeric duplexes and natural DNA are similar.

More complete information about the structure of the oligomeric complexes can be obtained with the aid of CD. As a consequence of the high sensitivity of the CD to the relative positions of the heterocyclic residues and the conformation of the monomeric units, the similarity of the CD spectra indicates the similarity of the geometrical parameters of the structures being compared. Thus the structural analogy of the triple-stranded $(Ap)_5A.2(Up)_5U$ and oligo(A).2poly(U) helices has been demonstrated with the aid of this method[9].

Comparison of the CD of the oligomeric complexes and natural nucleic acids of known structure is of particular interest. It was found that the CD spectra of complexes of oligoribonucleotides with one another or with oligodeoxyribonucleotides are of the non-conservative type characteristic of the *A* form of RNA in aqueous medium[10,53,86], while the CD spectra of the oligodeoxyribonucleotide complexes are similar to those of native DNA in the *B* form[53,87]. The CD spectra of the complexes formed by $d(pG–C)_n$ in solutions at a low ionic strength[69] and $d(pG–G–T).d(pA–C–C)_{2-4}$[18,89] are similar to those of DNA in the *B* form with a high content of the G:C pairs, while the CD spectrum of $d(pA)_3.d(pT)_{12}$[89] resembles that of DNA containing ~ 30% of G:C pairs. The CD method makes it possible to distinguish readily the different forms of oligomeric double helices in solution. The CD

spectrum of $d(C-G)_3$ in aqueous solution with a low NaCl concentration[32] resembles the spectrum of poly[d(C–G)]. .poly[d(C–G)] recorded under the same conditions and corresponding to the *B* form[90]. The addition of NaCl (up to 5 M) inverts the sign of the long-wavelength Cotton effect, which is associated with the transition of the oligonucleotide duplex to the left-handed *Z* form[32] [the existence of this form for $d(C-G)_n$ under the conditions of high ionic strength has been demonstrated by X-ray diffraction]. According to CD data, the *Z* form of $d(C-G)_2$ is unstable[32]. In the case of $d(A-T)_3(C-G)_3$, which forms a concatameric complex in which the $d(C-G)_n$ block is flanked by an alternating A–T sequence, the transition to the Z form is not observed according to CD data[32] [cf. the self-complementary d(C–G–C–G–A–A–T–T–C–G–C–G), which has been investigated by X-ray diffraction—see above].

The CD spectra have been calculated recently for numerous possible conformations of d(T–G–G–C–G–T–A–T–T–C–T). .d(A–G–A–A–T–A–C–G–C–C–A) and it has been shown that the CD amplitude at 275 nm varies linearly with the helix winding angle and the base pair twist[91]. The establishment of this correlation is important for the study of the dependence of the CD of nucleic acids on structural parameters.

According to modern ideas, the CD spectra of nucleic acids depend not only on the secondary molecular structure but also on the nucleotide sequence. Gray and Tinoco[92] developed a theory, according to which the form of the CD spectrum of DNA is determined by the interaction of mainly the neighbouring nucleotide pairs. Evidently the dependence of CD on the base sequence should be manifested particularly clearly at the level of oligomeric duplexes, because, in contrast to DNA, in the latter the frequencies of the encounters of specific combinations of two nucleotide pairs are not averaged out. Fig. 3 presents as an example the CD spectra of isomeric ribonucleotide duplexes[86]. The oligomeric duplexes with known sequences have been used in two investigations[86,93] to test the possibility of the determination of the nucleotide sequence of nucleic acids with the aid of CD. The contributions of all 10 combinations of two Watson–Crick nucleotide pairs have been isolated[86] on the basis of the analysis of the CD spectra of a series of oligonucleotide duplexes. The spectra obtained for the isomeric dinucleotide dimers differ sharply both in form and in amplitude. The CD spectra of the polymeric helices, constructed taking into account the spectroscopic contributions isolated, are in poor agreement with experimental curves. Hillen et al.[93] attempted to calculate the CD spectra of 12 restriction fragments of DNA with lengths ranging from 12 to 360 nucleotide pairs. For this purpose, use was made of a set of spectroscopic contributions of specific combinations of two nucleotide pairs taken from the spectra of synthetic double-helical polynucleotide (homogeneous or with repeating di- and trinucleotide sequences). The calculated and experimental spectra agree satisfactorily, with the exception of the positive CD band at 270 nm, which is particularly sensitive to conformational changes. The discrepancy is particularly notable for duplexes containing less than 43 nucleotide pairs apparently as a result of end effects.

3. Nuclear Magnetic Resonance

Together with the optical methods examined, NMR has been widely used recently in the study of the oligomeric complexes[24–27,39,46,52,58,59,87,94–106]. This method permits a detailed description of the steric organisation of the complexes in solution, the elucidation of the dynamics of the dissociation of the double-helical structures, and the estimation of the degree of structural analogy between the oligomeric duplexes and natural DNA and RNA. The overall effects accompanying the helix–coil transition are recorded with the aid of optical methods, while NMR makes it possible to trace the behaviour of individual base pairs.

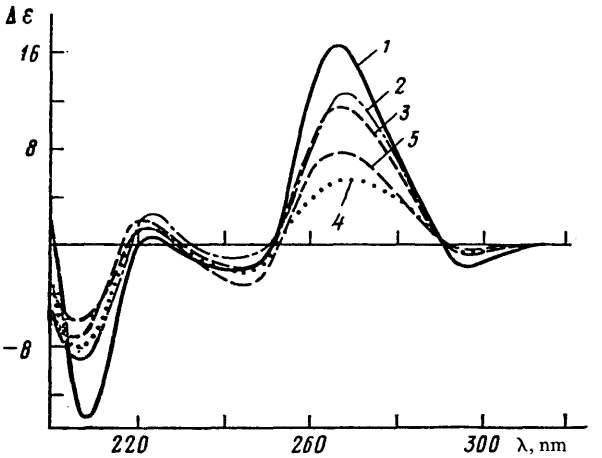


Figure 3. CD spectra of five double helical isomeric complexes containing four A:U and two G:C base pairs (1 M NaCl, pH 7.0, $c = 10^{-2}$ M per monomer unit): 1) A_2GCU_2; 2) A_2CGU_2; 3) U_2CGA_2; 4) $A_4G_2 + C_2U_4$; 5) $A_4CG + CGU_4$.[86]

It has now become possible to resolve and assign on high-class instruments (270, 300, 360, 500 and 600 MHz) the majority of the resonance signals of the protons of the bases and the sugar rings in double-helical oligonucleotides containing up to 12 pairs of bases and to reach a conclusion concerning the local environment of each proton. This made it possible to observe independently the changes in the character of the environment of each nucleotide pair of the duplex as the concentration, temperature, pH, etc. are varied. In the case of long nucleotide duplexes, the broadening of the resonance lines is associated with the rigidity of the polymeric nucleic acids, which prevents the rapid movement of the segments of the nucleotide chains in solution. The ^1H NMR spectra of a series of such duplexes, namely $A_{25}.U_{25}$,[107] $d(C_{15}A_{15}).d(T_{15}G_{25})$,[108] $dG_n.rC_{22}$, $dG_n.rC_{11}dC_{16}$, and $dG_n.dC_{22}$ ($n > 70$)[109], as well as two restriction fragments of DNA containing 43 and 69 base pairs[102], have been obtained, but the proton signals of the individual bases have not been assigned.

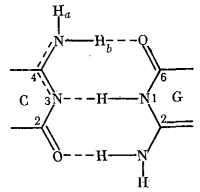
The ^{31}P NMR (145.7 MHz) spectra of oligonucleotide duplexes have been obtained recently[52,98]. They contain data concerning the conformation of the carbohydrate–phosphate skeleton of the oligomers forming the double helix. The breakdown of the "stacking" of the bases at temperatures exceeding the T_m of the duplex has been detected with their aid. In 1980 Cohen[103] analysed the ^{31}P NMR spectra of oligo d(G–C) obtained previously and suggested that the presence of two well resolved ^{31}P signals in 4 M LiCl and of a single signal at a low concentration of the salt indicate a left-handed *Z* form of the helix in these oligomers in a concentrated salt solution.

Two different groups of proton signals are investigated in order to obtain information about the structure of the oligomeric complexes.

(1) The signals of the non-exchanging protons linked to the carbon atoms of the heterocyclic bases or the sugar—the doublets of the H(5) and H(6) protons of the pyrimidine bases [the H(6) singlet in the case of thymine], the singlets of the H(2) and H(8) protons of the purine bases, the singlet of the CH_3 protons of thymine, and the signals of the protons in the sugar ring, mainly H(1'). They are all located in the range 4–9 p.p.m. relative to sodium 4,4-dimethyl-4-silapentanesulphonate (DSS). The spectra are investigated in D_2O or in buffer solutions containing D_2O. The positions of the oligonucleotide signals are determined as a rule by the standard "incremental assignment" method[26,27,110,111] by measuring the δ for the dimers, trimers, and other fragments of the given oligomer and assuming that the values of δ do not in the main change on passing to the intact oligomer. The chemical shift δ of the signal of each proton is subjected to the shielding influence of the neighbouring bases and also the bases in the complementary chain. Furthermore, the position of the signal is determined by the conformation of the furanose ring, the rotation of the base around the glycosidic linkage, the anisotropy of the phosphate group, and the interchain hydrogen bonds. Consequently δ depends on the structure of the double helix. On thermal dissociation of the complex, the signals of the non-exchanging protons of the bases shift both downfield and upfield[27]. Curves for the temperature dependence of the chemical shifts of the signals of the non-exchanging protons permit a direct determination of the thermodynamic characteristics of the helix–coil transition. Here one can trace the dissociation of each nucleotide pair of the duplex, although the assignment and measurement of the changes in the signals as a function of temperature remain a difficult problem.

(2) The signals of slowly exchanging ring protons of the imino-groups N(1)–H of guanine and N(3)–H of uracil (thymine), which are directly involved in the formation of hydrogen bonds between the bases (Watson–Crick pairs). The spectra are recorded in H_2O or in aqueous buffer solutions. The N(1)–H resonance signal of guanine characterises the G:C pair and the N(3)–H signal of U (T) characterises the A:U(T) pair. We may note that the resonances of the imino-group protons of the free oligomers are not observed in water owing to the rapid exchange between the protons with the solvent. The formation of a hydrogen bond leads to a slower exchange of the protons with water and to the appearance of resonance signals in the region of weak fields (12–15 p.p.m. relative to DSS). The presence of such signals in the ^{1}H NMR spectrum of short oligonucleotides is convincing evidence for the formation of a duplex. With increase of temperature, an upfield shift and a broadening and disappearance of the signals, associated with the increase of the relative content of the open-chain forms and the rapid exchange of the imino-group protons in the open-chain form with water, are as a rule observed. The temperature of the disappearance of the signal is not related to the thermodynamic stability of the double helix and yields only comparative characteristics of the stabilities of different nucleotide pairs of the duplex, because the resonance signals of the N(1)–H protons of G and the N(3)–H protons of T (U) are markedly broadened even at a concentration of the open-chain forms of ~ 10% and cannot be traced further. The observation of the behaviour of the individual signals on gradual increase of temperature helps in their assignment[27,52,99,112]. Here account is taken of the fact that the resonance of the proton of the imino-group of the "isolated" G:C pair is observed in a stronger field (13.6 p.p.m.) than the corresponding resonance of the A:T pair (14.6 p.p.m.).[96] A procedure involving chemical modification is sometimes used in the assignment[99] or the calculated and experimental chemical shifts are compared[27]. When triply-stranded oligomeric complexes are formed, the signals of the imino-group protons corresponding to the formation of "reverse" Hoogsteen A:U pairs are observed[27,104] in addition to the signals of the exchanging protons of the Watson–Crick pairs in the range 14.6–15 p.p.m.

The signals of the exchanging protons of the imino-groups of the C(4)–NH_2 base of cytosine and the C(2)–NH_2 base of guanine, located in the range 6–9 p.p.m. relative to DSS, are considered together with the protons of the imino-group. The exchange of the amino-group protons with the solvent is slower than that of the imino-group protons[98]. The partial double bond character of the C–NH_2 linkage in cytosine restricts the rotation of the amino-group and therefore at low temperatures individual broad signals are observed for each of the protons of the NH_2 groups of cytosine. In complementation interactions the signal of the proton involved in the formation of a hydrogen bond (H_h in the scheme below) shifts downfield, whereas the signal of the proton accessible to the solvent (H_a) undergoes an upfield shift. For guanine, a single resonance signal due to the two protons of the amino-group is observed, which is explained by the rapid rotation of the latter about the C–NH_2 bond.



On formation of the complementary pair, the average signal of the NH_2 protons of guanine shifts downfield. The dependence of the chemical shift of this signal on the nucleotide concentration can be used to estimate the equilibrium complex formation constant for the dinucleotides[58,63]. Furthermore, by analysing the temperature dependence of the width of the proton signals of the amino-groups in cytosine and guanine, it is possible to discover if the rotation of the amino-group about the C–NH_2 bond in the oligomeric duplexes is rapid or slow[98]. It is noteworthy that these signals are more often used to detect the formation of complementary complexes between dinucleoside phosphates (dinucleotides)[58,63,64].

Detailed ^{1}H NMR study of the structural characteristics of a number of oligomeric systems showed that complexes containing the d(A–T–G–C–A–T)[96,113], d(pG–C)$_4$, d(pT–A)$_{3,4}$, d(pA–G)$_4$.d(pC–T)$_4$,[112] d(A–A–A–G–C–T–T–T)[114], d(C–C–G–G), d(G–G–C–C)[98], d(G–G–A–A–T–T–C–C)[52], d(A–T–C–C–T–A–T–A–G–G–A–T)[99], d(C–T$_5$–G).d(C–A$_5$–G)[27], and d(A–A–T–T–G–C–A–A–T–T)[106] deoxyribonucleotide units assume in solution a conformation close to that of the *B* form of DNA, while the geometry of the *A*(*A'*) form of RNA is characteristic of the complexes of the ribo-derivatives A–A–G–C–U–U[26,97], C–C–G–G[96], and A–G–C–U[105] as well as the d(C–T$_5$–G).r(C–A$_5$–G) hybrid derivatives[27]. This conclusion was reached as a result of a comparison of the calculated and experimental chemical shifts for the exchanging and non-exchanging protons of the bases of a given nucleotide pair of the oligomeric complex. In the calculation of the chemical shift, the influence of the magnetic fields of the ring currents on the signals of the corresponding protons was determined (without taking into account the influence of

other factors) for all possible combinations of the neighbouring base pairs, taking into account the known geometrical parameters of the *A*, *B*, and *D* forms of DNA[112,113,115]. One should bear in mind that agreement between the calculated and experimental chemical shifts of the signals of the exchanging protons is by no means always observed[27] and frequently only for the inner pairs of bases in the duplexes[95,96,98,112,114]. Signals of the protons of the end pairs are in a stronger field than required by the calculation. According to a number of investigators[95,112,114], equilibrium between the hydrogen-bonded and open forms are characteristic of the end nucleotide pairs of the duplexes (the signals of the open form were manifested in a stronger field) and the chemical shift of the signals of the imino-group protons is determined by the ratio of the populations of the two forms. An alternative explanation of the upfield shift of the signals of the exchanging protons in the terminal nucleotide pairs is the formation of intermolecular structures as a result of the "stacking" of the ends of the oligomeric duplexes[98]. A discrepancy between the calculated and experimental values of δ has been noted also for the non-exchanging protons of the terminal pairs and has been attributed to the stacking interaction of the ends of the duplexes[52,98]. In a study of the double helical A–G–C–U and A–C–G–U, the δ for the non-exchanging protons of the bases were calculated much more rigorously[105]. The calculated and experimental δ for the majority of the non-exchanging base protons of A–C–G–U did not agree, in contrast to its isomer. The authors concluded that the double helix in A–C–G–U is a non-standard form, and emphasised the importance of this conclusion for the estimation of the conformational possibilities in the RNA duplexes.

The conformation of the furanose rings in the nucleotide units of the complex, which determines the form of the double helix, has also been established with the aid of ^{1}H NMR data. For this purpose, measurements were made of the spin–spin vicinal coupling constants of the protons at C(1′) and C(2′) and were compared with the values predicted for different conformations of furanose. It was found that, for all the carbohydrate residues in d(A–T–G–C–A–T)[113], d(C–C–G–G), and d(G–G–C–C)[98], under complex formation conditions, the C(3′)-*exo*-conformation is characteristic of DNA in the *B* form. The two deoxyribose residue in the d(C–T_5–G).d(C–A_5–G) duplex, belonging to d(C–A_5–G), are 90% in the C(2′)-*endo*-conformation and the double helix therefore has the geometry of the *B* form[27]. In contrast to these systems, the furanose rings of all the monomeric units of the complex formed by A–A–G–C–U–U[26] or all the monomeric units of the ribo-chain of the d(C–T_5–G).r(C–A_5–G) complex[27] are in the C(3′)-*endo*-conformation characteristic of RNA in the *A*(*A*′) form[26]. Analysis of the temperature variation of $J_{1',2'}$ led to the conclusion that the C(3′)-*endo*-conformation of the furanose rings predominates, so that the helices in the duplexes formed by C–A–U–G[111] and A–G–C–U[105] and also in G–A–G–C.G–C–U–C[110] have the *A*(*A*′) form.

Additional information about the secondary structure of the oligomeric complexes was obtained in the study of the interaction with the antibiotic actinomycin D of the double helices enriched in G:C pairs. A characteristic property of this antibiotic is its specific binding to DNA in the *B* form and its lack of affinity for RNA and hybrid helices[116]. It was shown by ^{1}H NMR that the phenoxazinone ring of actinomycin D is inserted between the G:C pairs of the double helical oligodeoxyribonucleotides[96,112,117,118], which indicates a DNA-like conformation of such complexes in aqueous solution.

The formation of the A–G–C–U or A–C–G–U duplexes[105] entails a change (by 20° and more) of the glycosidic angle of twist in the adenosine and cytidine residues. This was demonstrated by analysing the δ for the anomeric H(1′) protons.

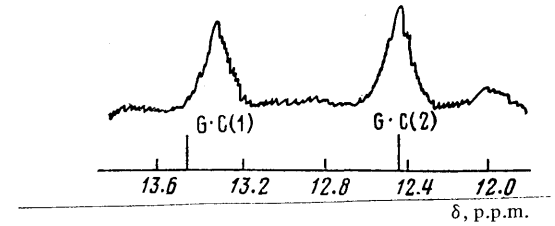


Figure 4. NMR spectrum (220 MHz) of the exchanging imino-group protons of the guanine residues in the duplex

CpCpGpG
GpGpCpC
1 2 3 4

at 0 °C in water. The calculated positions of the resonance signals, subject to the condition that the structure of the double helical CpCpGpG corresponds to the structure of RNA-11, are indicated by lines[95].

The study of the temperature variation of the chemical shifts and the signal widths of the exchanging protons of the oligomeric duplexes led Patel and coworkers[52,94,117] to the conclusion that, under the conditions of the thermodynamic stability of the helix, there is a probability of the incomplete bonding of the terminal nucleotide pairs in such systems (regardless of the nucleotide composition and sequence). In other words, the rapid formation and rupture of the hydrogen bonds between the bases of the terminal nucleotide is postulated, the equilibrium shifting towards an increase of the relative content of the open forms with increase of temperature. The rapid formation and dissociation of nucleotide pairs at the ends of the double helix ("fraying") is much faster and occurs at a lower temperature than the thermodynamic fusion–separation of the strands of the duplex, and leads to an average resonance signal whose chemical shift and width are determined by the ratio of the open forms and the forms stabilised by hydrogen bonds. Fig. 4 presents the ^{1}H NMR spectrum of the duplex formed by C–C–G–G at 0 °C. The calculated positions of the proton signals of the terminal and inner G:C pairs are indicated by lines. If it is assumed that the upfield shift and the broadening of the signals due to the protons of the terminal G:C pairs are due to the increase of the relative content of the open forms, it is found that at 0 °C the terminal base pairs C–C–G–G.C–C–G–G are "fused" to the extent of 8%.[95] The analogous analysis of the ^{1}H NMR spectrum of the duplex formed by d(A–T–G–C–A–T) leads to the conclusion that, under the conditions of the stability of the double helix, the bases of the A:T end pairs are in the open form to the extent of 15%.[96] With decrease of temperature, the signals of the imino-group protons of the A:T and T:A pairs of the double helical d(A–T–G–C–A–T) undergo a downfield shift; the displacement of the signals of the protons of the terminal A:T pairs of the duplex is observed down to −30 °C (in aqueous methanol) and that of the signals of the inner T:A pairs is observed down to −20 °C. Patel and Hilbers[94] interpreted this as an increase of the fraction of the hydrogen-bonded forms with decrease

of temperature. According to their calculations, at 3 °C the fraction of the open forms is 22.5% for the terminal A:T pairs and 1.1% for the inner T:A pairs, being absent for the central G:C pairs. With increase of temperature, the reverse process, namely a successive increase of the relative content of the open forms (initially the terminal and then the inner nucleotide pairs undergo ring opening) is observed for oligonucleotide complexes of any composition and with any sequence[27,94,95,99,112]. Fig. 5 presents the ^{1}H NMR spectra of the complex formed by A–A–G–C–U–U in the region of a weak field at different temperatures. At 1 °C the absorption lines of the imino-group protons are observed at 13.2, 13.5, and 14.2 p.p.m. (each signal corresponds to two identical resonances of the imino-group protons of equivalent nucleotide pairs). With increase of temperature, all three signals are broadened and disappear in the following sequence: initially the signal at 13.2 p.p.m., to which correspond the terminal A:U pairs, then the signal at 14.2 p.p.m. associated with the inner A:U pairs, and finally the signal at 13.5 p.p.m. associated with the central G:C pairs[97]. Thus the signals of the less stable (owing to the incomplete pairing) terminal A:U pairs are broadened and disappear faster than the signals of the inner A:U and G:C pairs shielded from the effect of the solvent. In the d(A–T–C–C–T–A–T–A–G–G–A–T) duplex fusion also begins from the ends of the double helix. There is no preliminary fusion of the central A–T fragment, i.e. the sequence of four A:T pairs, protected by the G:C pairs, is too short for the local destabilisation of the duplex[99].

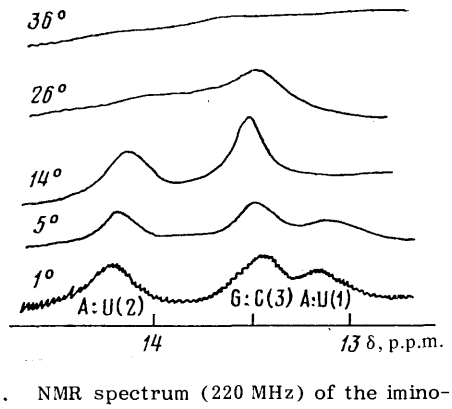


Figure 5. NMR spectrum (220 MHz) of the imino-group protons of the duplex

ApApGpCpUpU
· · · · · ·
UpUpCpGpApA
1 2 3 4 5 6

at different temperatures in H_2O (1 M NaCl, pH 7.6).[97]

In the study of the temperature variation of δ of the non-exchanging protons, the T_m of individual nucleotide pairs of duplexes were determined and it was shown that they depend on the composition and sequence of the bases. On dissociation of the double helical oligonucleotides without terminal G:C pairs, namely d(A–T–G–C–A–T)[51] and A–A–G–C–U–U,[26] the stability of the nucleotide pairs increases in the following sequence: terminal A:U(T) pairs < inner A:U(T) pairs < central G:C pairs. The tendency of the terminal pairs to undergo "differential" melting (i.e. before the melting of the remainder of the duplex) is greatly reduced for the duplexes in which the A:U pairs are internal and the more stable G:C pairs are terminal. Thus stepwise dissociation is not observed (the helix–coil transition takes place in accordance with the "all or nothing" principle[27]) for the C–A–U–G[111], G–A–G–C.G–C–U–C[110], d(G–G–A–A–T–T–C–C),[52] and d(C–A_5–G).d(C–T_5–G)[27] duplexes, as well as C–C–G–G which is made up exclusively of G:C pairs[95] and the T_m of the individual nucleotide pairs, determined with the aid of ^{1}H NMR (of the non-exchanging protons), corresponds to the T_m of the helix obtained by optical methods. On the other hand, the above tendency increases sharply for the d(pT–A)$_3$ duplex: at 5 °C the nucleotide chains are retained mainly via two central A:T pairs[100]. The result of studies of the A–G–G–A.U–C–C–U and U–G–C–A duplexes whose terminal A:U pairs melted at the same temperature as the inner G:C pairs[59], are in some conflict with these data. For the same nucleotide composition and the same number of inner G:C pairs in the A–G–C–U and U–G–C–A duplexes, the terminal residues are dissociated in the former but not in the latter[59]. Finally, the dissociation of the terminal pairs diminishes in the presence of unpaired (looped) bases[59] (see above). This information is useful for the understanding of the nature of the RNA–RNA interactions in the cell. In the study of the duplexes formed by the self-complementary d(G–G–C–C) and d(C–C–G–G), Patel observed a difference between the temperature variations of δ of the non-exchanging protons of the inner and outer G:C pairs[98]. He believes that these differences are due to "end to end" aggregation of the duplexes resulting from the stacking interactions of the end pairs and leading to a greater shielding of the protons of these pairs. As a result, the signals of the protons of the terminal G:C pairs are observed in stronger fields. With decrease of temperature, they continue to shift upfield (without reaching a plateau) and the T_m determined with their aid is smaller than the T_m for the inner pairs. It is noteworthy that the quantitative aspects of the analysis of the temperature variations must be approached with caution, since the T_m determined from the temperature variations of the signals of different non-exchanging protons within the limits of the same nucleotide residue sometimes differ appreciably[7]. The error in the determination of T_m is smaller for the duplexes formed by non-self-complementary oligonucleotides, since in this case one can take into account the temperature variation of the protons of each chain[27]. In the description of the "differential" fusion of the terminal nucleotide pairs of oligomeric duplexes, some workers unjustifiably used the term "fraying" of the ends[59,100,110], which reflects a kinetic effect (see above) and is in no way related to the equilibrium concentration of the open and hydrogen-bonded forms[27]. For example "fraying" of the ends occurs in d(C–T_5–G).d(C–A_5–G), but the duplex does not decompose and the content of the partly fused forms is very low[27].

A study[99] of the duplex d(A–T–C–C–T–A–T–T–A–G–G–A–T), containing one non-complementary T:T pair, provides a good illustration of the possibilities of the NMR method. It was shown that the tridecanucleotide forms a regular structure similar to DNA in the *B* form and that the non-canonical T:T pair does not emerge from the helix. However, it is of interest that the incorporation of the T:T pair diminishes appreciably the overall stability of the double helix as a result of the formation of an additional unstable region where fusion begins as well as in the terminal sections, as can be seen from the disappearance of the signals of the exchanging protons.

The NMR study of the relaxation behaviour of the resonances of the exchanging protons of the bases of an oligomeric duplex, namely the 12-unit restriction fragment d(C–C–G–C–A–C–T–G–A–T–G–G).d(C–C–A–T–C–A–G–T–G–C–G–G), was carried out recently for the first time[101]. Analysis of the rates of relaxation and of their temperature variation made it possible to examine a completely new aspect of the behaviour of the duplexes—the conformational fluctuations of the helix. The absence of internal dynamics in the 12-unit DNA fragment, at least on the 10–100 ns time scale, was observed[101]. It was shown that there is no reorientation of the bases (relative to the axis of the helix) and that this fragment can be regarded as a rigid rod. Furthermore, a remarkable observation was made concerning the mechanism of the opening of the individual base pairs. It was found that the exchange of the imino-group protons of the thymine residues with the solvent at 30–40 °C is not accompanied by the opening of the neighbouring G:C pairs. On this basis, the authors[101] concluded that the rates of the random opening of the A:T pairs in any DNA are independent of the nucleotide sequence and length and are therefore identical for all types of DNA. This conclusion has been confirmed experimentally in the study of the restriction fragments of DNA consisting of 43 and 69 units[102].

In a number of ^{1}H NMR studies of the complex formation by oligomers, detailed investigations were made of the kinetic aspects of the exchange of the imino-group protons with water[24,25,97]. These data made it possible to estimate the lifetime of the base pairs in the helical complex and to obtain independently the kinetic parameters of the initiation and propagation of the oligomeric double helix[25]. The calculated activation energies and rate constants for nucleation and dissociation agree well with the corresponding data obtained for ribo-oligonucleotides with the aid of the temperature jump method (Section V). The exchange process responsible for the broadening of the resonance lines can be described as follows in general terms[24,114]:

$$NH_h \underset{k_{ch}}{\overset{k_{hc}}{\rightleftarrows}} NH_c \xrightarrow{k_{H_2O}} H_2O \ .$$

According to this scheme, the imino-group protons can exist in one of three states: within the double helical structure (NH_h), in the open form (NH_c), and as part of the H_2O molecule. The equilibrium constant of the transition from the hydrogen-bonded (h) to the free (c) state is $K_{eq} = k_{hc}/k_{ch}$. The characteristics of these exchange processes are now well known[119]. Equations describing the relations between the widths and positions of the resonance lines of the double-stranded complex and the rates of the exchange reactions have been derived[52,97,119]. Further details of the mechanism of the exchange of the imino-group protons with water have been reported[24,119].

4. Column Chromatography

Oligonucleotides immobilised on a carrier can form complexes with complementary homogeneous[120–122] and heterogeneous[121,123] oligonucleotides (including the formation of hybrid ribodeoxyribonucleotide complexes[120,121]). Cellulose[120,121,123], hexamethylenediamine-Sepharose[123] to which the oligonucleotide was linked covalently, and DEAE-cellulose, in which the irreversible sorption of the oligonucleotide linked covalently to a soluble polymer [poly(vinyl alcohol)] has taken place[122], are used as carriers. Under temperature gradient conditions, the complementary oligonucleotide is desorbed and the stability of the complex can be estimated approximately from the temperature at which the peak emerges. It has been shown that all the bases of the immobilised oligomer participate in the formation of hydrogen bonds[120,121] and that this process is highly specific: a single non-complementary pair is sufficient to prevent the sorption of the oligonucleotide[124]. Chromatography on carriers with oligonucleotides is discussed in the literature mainly as a method for the separation of oligonucleotide mixtures[120–123].

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The Structure of Simple Liquids

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Theories of the structure of simple liquids, and the present state of the problem, have been examined. Attention has been paid to the unity of the static and dynamic characteristics of the structure. New results obtained by molecular-dynamic computer modelling, including the use of the ideas of statistical geometry, have been presented. The lack of justification for the quasi-crystalline approach to the structure of short-range order, and the fruitfulness of Bernal's ideas, have been pointed out.

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I. INTRODUCTION

A large amount of information on the properties of different liquids has been obtained in the last ten years. The number of liquids is very large, and is increasing continuously as a result of the synthesis of new compounds. The selection of substances for practical application requires their physico-chemical "classification", and this is becoming more difficult. A reasonable approach involves the use of sufficiently general regular features relating molecular structure to the properties of matter. Considerable progress has been made in reducing the amount of primary information needed by the use of the theory of physical similarity (the generalised law of corresponding states)[1,2].

A liquid, unlike a gas, is a collection of strongly interacting particles. It is distinguished from a crystal by the irregularity of its structure. Since it has not been possible to select a suitable simple model of a liquid, attempts have been made to bring it so "close" to either a gas or a solid crystal that the results based on the corresponding ideal model can be applied to a significant extent.

II. THE SEARCH FOR SIMPLE MODELS

In 1869, the detailed experimental work of Andrews[3] finally established the existence of the critical point (CP) of the liquid–vapour equilibrium as a universal property of matter. Andrews formulated the principal physical consequences of this fact: the possibility of a continuous change from a gas to a liquid in the region of the critical point; the existence of intermediate states above the critical point, which cannot be confidently assigned to any of the states of aggregation, and the unique character of transitions beyond the critical point. Van der Waals' thesis, which appeared four years after the publication of Andrews' work[3], contained

the elementary theory of the gas–liquid state in a very lucid form. Qualitatively, it showed satisfactory consistency with Andrews' discovery.

Boltzmann, in his review "Vorlesungen über Gastheorie"[4], discussed in detail the physical significance of van der Waals' equation and its many consequences. He pointed out the existence of intermediate states of matter in a continuous change from a gas to a liquid. Boltzmann's achievements in the development of the kinetic theory of gases stimulated studies in which the description of liquids was approached "from the direction of the gas".

These achievements provided a basis for bringing a liquid "closer" to the gaseous state (dense fluid states, and not an analogy between a liquid and a rarefied gas, were of course assumed). The range of applicability of the model of a weakly interacting gas was extended to an unjustifiable degree, however, and this led to the concept of the unstructured state of liquid. Experiments on the observation of the scattering of X-rays at small angles[5] (Stuart, Danilov, and their successors) demonstrated convincingly the existence of local ordering of the molecules of a liquid. For an arbitrarily chosen molecule, the neighbours in the first and second layers lie on the average at definite distances; the average number of neighbours in these layers can also serve as a characteristic of the short-range order in a liquid (the coordination number).

The breakdown of the view that liquids are unstructured was used, together with other arguments, to strengthen the position of the "solid" (quasicrystalline) model. This approach was developed most fully by Frenkel in 1945 in a monograph[6] which established an epoch in the physics of liquids. Many experimental facts received a simple explanation. It became possible to carry out elementary estimates of kinetic phenomena in liquids, and this stimulated studies in various branches of physical chemistry. This approach also has significant unsatisfactory features, however, particularly in the study of the structure of liquids, which is often interpreted as quasicrystalline. There is no satisfactory definition of quasi-crystallinity. The term combines a broad spectrum of concepts, from regularity in the arrangement of the atoms, disturbed by thermal motion, to a microcrystalline heterogeneous structure (the microcrystallinity is "softened", and the indefinite concepts of cybotaxes and clusters are introduced).

The adherence of many research workers to quasicrystalline models of liquids is strengthened by the established traditions of the processing and interpretation of the results of diffraction experiments. On the basis of an approximate form of the radial distribution function (RDF), conclusions are reached about the degree of correspondence between the structures of the liquid and the crystal. Although information about the average number of neighbours in the first coordination spheres and about the position of these spheres (layers) is reliably established from the processing of the X-ray diffraction patterns, the investigation of the finer details of the structure comes up against the indeterminate nature of the method. The RDF transforms the three-dimensional distribution of the atoms into a smoothed one-dimensional function. This imposes a fundamental restriction on the possibility of using the method to interpret the structure of the short-range order in a liquid: practically identical RDF can correspond to quite different configurations.

The concept of the quasicrystallinity of liquids does not follow from experimental data, but is rather related to an *a priori* underestimation of the unique character of the dense irregular structure. The existence of long-range order presupposes a quite definite type of short-range order. In the absence of the requirement of regularity (and when there is a certain free volume), the system has access to a new and extensive region of configuration space, and the system spends almost all its time in this region.

Quasicrystallinity is apparently a concept which is just as unacceptable as the unstructured dense liquid picture. Bernal was the first, in the late nineteen-fifties, to begin the battle against these concepts. He concluded that "this short-range order" is "quite different from what might be expected from an analogy with the crystalline state"[7]. Using "natural" (mechanical) models, Bernal demonstrated the existence (and even predominance), in a close-packed random structure, of elements of local ordering which are known to exclude the possibility of the appearance of a regular structure. Bernal's work will be examined in more detail below.

The next major achievement in the study of the structure and properties of simple liquids was associated with the use of the hard sphere model as an object of study by the methods of statistical physics and computer simulation. In this model, the forces of attraction between the particles is neglected, and the repulsion is described by the pair potential of inter-particle interaction $\Phi(r)$, which has the form of a rectangular wall

$$\Phi(r) = \begin{cases} \infty & \text{for } r < \sigma \\ 0 & \text{for } r \geqslant \sigma \end{cases} \qquad (1)$$

Here, σ is the diameter of the sphere, $v_0 = 1/6\pi\sigma^3$ its volume, $\rho/\rho_0 = Nv_0/V$ the proportion of the volume of the system occupied by the spheres (the density of packing), and V the total volume of the system. Allowance for thermal motion in the hard-sphere model leads to a linear temperature dependence; the RDF depends only on the density. The average potential energy of a system of N hard spheres is equal to zero, and the internal energy U is independent of the volume and can be written as for an ideal gas in the form

$$U = 3/2Nk_BT$$

It should not be thought that the theoretical description of the equation of state and the structure of this model is simple. The complexity of the problem is due to the fact that for dense states, the total volume of the spheres makes up a significant proportion of the total volume of the system. The simplicity of the model is sufficient, however, to permit the effective use of the Percus–Yevick approximation and the hyperchain approximation in the theory of correlative functions[8] and to bring the calculations to numerical values. Fig. 1 shows the RDF for "dense" argon, obtained experimentally[9] and calculated by the Monte Carlo method for the hard sphere model[10].

The RDF in the hard sphere model reproduces qualitatively the RDF of a real simple liquid. The dependence of the structural characteristics of the model on the curvature of a Lennard-Jones type potential in the range of small distances has been studied[10]. The splitting of the second peak of the RDF, which is observed for a system of hard spheres (see Fig. 1), takes place at values of the exponent of the repulsive part of the potential $n \geqslant 75$, whereas the average number of nearest geometric neighbours in the hard sphere model differs by less than 0.1% from the corresponding characteristic of systems with $n \geqslant 25$. This may indicate that the "geometric" factor has a decisive role in the formation of the irregular compact structure.

Before continuing the examination, it is appropriate to investigate how clearly and completely it is possible to formulate the actual concept of "the structure of liquids". This concept is much broader and deeper than any static

geometric representation. The structure of a molecular system is related to and forms a unity with the thermal motion. An "instantaneous photograph" of a single crystal at a high temperature, fixing the position of its particles, shows little similarity to the structure of the ideal lattice. An approximation to this structure is achieved by increasing the exposure time and averaging the configurational picture. The case of a liquid is even more complicated, because of the constant drift of particles from their immediate environment, and individual motion. Direct photography will give a picture which will become increasingly blurred with increase in the exposure. There arises the question of how to determine the characteristic geometric representation of the liquid in this case. It can be constructed by analysing the dynamic set of configurations formed by the particles of the system in thermal motion. Thus in the examination of the structure of a liquid, the treatment cannot be restricted to the geometric aspect. It is necessary to take into account the dynamic properties of the liquid. Its structure is revealed in different ways in time intervals of different scale.

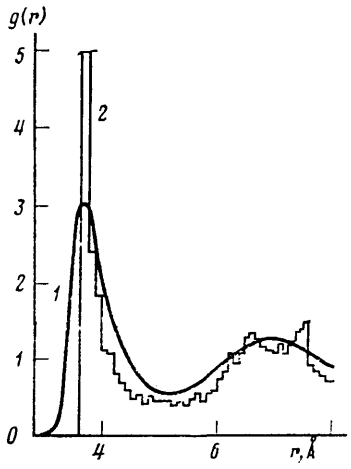


Figure 1. Radial distribution function of liquid argon: *1*) experimental, from elastic neutron scattering at 85 K,[9] *2*) histogram giving the result of a calculation by the Monte Carlo method for the hard sphere model[10].

III. THE STRUCTURE AND DYNAMIC PROPERTIES OF A LIQUID

1. Structure-sensitive Properties

In physicochemical analysis, the concept of "structure-sensitive" properties is often used, but attention is not always paid to which structural aspect is being revealed in the change in the given property. For example, the electrical conductivity of crystalline copper at room temperature is "sensitive" chiefly to constant defects of the structure and the difference between the instantaneous configuration of the ions and their regular average arrangement. With decrease in temperature, the positional "blurring" decreases, and the electrical conductivity σ_e increases. At 5 K it is ~1.5×10^4 times that at 300 K, and ~8.4×10^4 times that close to the melting point (1356 K). Compared with this difference, the change in σ_e on fusion is slight ($\sigma_e^l/\sigma_e^{cr} \cong 2.04$), and indicates a certain similarity between the instantaneous configurations of the liquid and the crystal at a high temperature. The electrical conductivity is a macroscopic characteristic, and represents a certain average value of microscopic variables of the crystal system, but from the structural viewpoint this averaging reflects the degree of irregularity in the "series" of successive configurations. For a macroscopic equilibrium specimen, the averaging of any local characteristic with time is equivalent to averaging with respect to the volume, since in the volume the system contains a vast number of independent sub-systems (microvolumes with linear dimensions greater than the de Broglie wavelength).

An example of a physicochemical property determined by positional and orientational ordering of the particles is the anisotropy. It is characteristic of crystals of low symmetry, and is not shown by ordinary liquids.

The heat capacity is another structure-sensitive property. In compact condensed systems, the heat capacity is determined by the spectrum of the frequencies of the elastic vibrations of the atoms; the main contribution is made by high-frequency modes. The influence of structure on the properties is due to a change in the spectrum of the vibrations in structural rearrangements, and also to a change in the contribution of individual motions to the energy characteristics† of the system. There is no simple relationship between them.

The dynamic structure of a liquid[11] (in momentum space) is related to the configurational structure. Experimental methods exist for the study of the dynamic structure, for example from scattering of neutrons by matter. By determining the elastic (without change in wavelength and energy) and inelastic coherent scattering on the one hand, and the inelastic noncoherent scattering on the other, it is possible to separate the contributions made to the scattering by the collective and individual motions of the particles.

2. The Fluctuational Aspect of Structure

The RDF is the most widely used primary characteristic of the structure of liquids. It is usually found from experiments on the low-angle scattering of X-rays. The scattering power of a liquid as a function of the angle of scattering θ is proportional to the static structure factor ($S(k)$, which carries the necessary information on the averaged configurations of the particles in the volume:

$$I/I_0Nf^2 = S(k)$$

Here, I_0 and I are the intensities of the exciting and scattered radiation respectively; N the number of atoms in the scattering volume V; f the atomic scattering coefficient, which depends on the electron density; $k = (4\pi/\Lambda) \times \sin(\theta/2)$ the modulus of the wave vector of the scattering; and Λ the wavelength of the X-rays.

The expression for the RDF is obtained from $S(k)$ by means of a Fourier transformation:

$$g(r) = 1 + \frac{1}{8\pi^3\rho}\int [S(\mathbf{k}) - 1]\exp(-i\mathbf{kr})\,d\mathbf{k}$$

Here, $\rho = N/V$ is the average numerical density.

†On the fusion of polyatomic (molecular) crystals, the heat capacity may also increase as a result of the removal of the degeneracy from rotational and librational degrees of freedom.

As noted earlier, the RDF gives extremely crude (contracted) information on the structure of a liquid. The important feature for scattering is the non-uniformity of the distribution of the scattering centres (molecules) with respect to the elementary volumes ΔV_i, the linear dimensions of which are of the order of the wavelength of the radiation; N_i is the number of molecules in the volume ΔV. The total effect of scattering with allowance for interference depends on the average value of the non-uniformity $\langle (N_i - \bar{N}_i)^2 \rangle^{1/2}$ in these volumes#. By changing the wavelength of the radiation or the angle of scattering (that is **k**), it is possible to "probe" non-uniformities of different scale. Essentially, the fluctuations in the density and their correlation in the thermal motion are being revealed here. Thus the structure factor, and hence the RDF, carry chiefly the information on the structure of the liquid which is contained in its description in the language of fluctuations. In the long-wave limit, the following relationship exists between the average value of the fluctuations $\langle (\rho - \bar{\rho})^2 \rangle / \bar{\rho}$ and the structure factor of RDF:[12]

$$\lim_{k \to 0} S(k) = 1 + \rho \int [g(r) - 1] \, dV = V \langle (\rho - \bar{\rho})^2 \rangle / \bar{\rho} \qquad (2)$$

On the other hand, statistical thermodynamics makes it possible to express the density fluctuations (naturally, long-wave compared with the internuclear distance) in terms of the isothermal compressibility of the substance $\beta_T = V^{-1} \cdot (\partial V / \partial p)_T$:

$$\langle (\rho - \bar{\rho})^2 \rangle / \bar{\rho}^2 = k_B T \beta_T / V \qquad (3)$$

The quantity β_T can be regarded as a function of the response to a small static perturbation of the system by pressure. It is clear from Eqn.(3) that the response function becomes large where the fluctuations are large, for example close to the critical point of the liquid–vapour equilibrium. Eqns.(2) and (3) can be generalised to the case of short-wave perturbations§ with wavenumber k:[12]

$$S(k) = \rho k_B T \beta_T(k) \qquad (4)$$

Here, $\beta_T(k)$ is the isothermal response function, which depends on k and which characterises the isothermal compressibility for short-wave perturbations.

Liquid argon or sodium are regarded as typical simple liquids. Close to the melting point, the structure factor of liquid argon does not differ greatly from $S(k)$ for liquid sodium (see Fig.2). The structural similarity between the liquid inert gases and the alkali metals was unexpected, since their forces of interaction are quite different. The existence in metals of a sub-system of almost free electrons alters the situation in many respects, for example by leading to the appearance of a long-range oscillating component in the effective potential of the paired interaction $\bar{\phi}(r)$.[12,13] Without going into details, it is found that the structure of the short-range order in a dense liquid is not appreciably sensitive to the form of the function $\phi(r)$. Its similarity to the structure of a system of hard spheres indicates the important role of the "geometric" factor (short-range repulsion forces) in the production of the short-range order of simple liquids. This is also indicated by the one-parameter thermodynamic similarity in the fusion curves of the inert gases and typical metals[14].

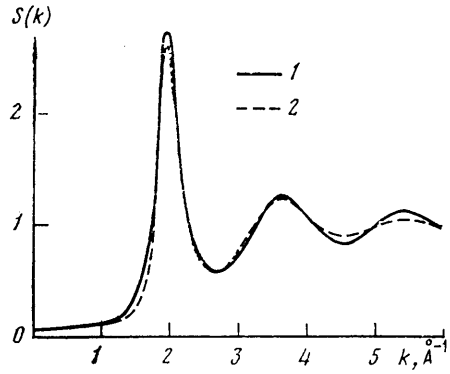


Figure 2. Structure factor for liquid argon at ~85 K [9] (*1*) and for liquid sodium at ~383 K [15] (*2*), close to the melting point.

It is not possible in the present review to carry out a detailed examination of the fluctuations and correlation functions. It is necessary, however, to distinguish the "fluctuational aspect" of the structural description of liquids. It is reflected in condensed form by Eqns.(2)–(4), from which it follows that the spectrum of the density fluctuations contains important information on the supermolecular structure. The dynamics of the fluctuations, the characteristic time of their dissipation, self-diffusion, and collective modes are all related to the structure of the liquid in the broad sense. The positions of two close molecules are statistically correlated not only in space but also in time. The Van't Hoff function $G(\mathbf{r}, t)$ is introduced as the average numerical density of the particles¶; close to the point **r** at moment of time t with the condition that the origin of coordinates coincides with one of the particles at $t = 0$. This function can be used to describe the space–time correlations. To change from $G(\mathbf{r}, t)$ to the RDF, it is necessary to fix the time and put $g(r) = G_d(r, 0)$; $G_d(r, t) = G(r, t) - G_s(r, t)$, where $G_s(r, t)$ is the auto-correlation part of the Van't Hoff function.

Just as the spatial fluctuation of the density represents a superposition of harmonic vibrations of different wavelength, the time "portrait" of the correlation can be expressed by a definite frequency spectrum (ω), using the Fourier transformation of the function $G(r, t)$ relative to the time t. This introduces the dynamic structure factor $S(k, \omega)$:

$$S(k, \omega) = \rho \iint \exp[-i(\mathbf{kr} - \omega t)] \, G(\mathbf{r}, t) \, d\mathbf{r} dt$$

#The angle brackets or the bar above the letter denote averaging with respect to the ensemble.

§In the present work, the letter k is used to denote both the wave vector of scattering and the Fourier components in the representation of the spatial density distribution by the set of harmonic functions $\rho(\mathbf{k})$ with different wavelength λ, $k = 2\pi/\lambda$. The condition of the first interference maximum when scattering is observed relates the quantities λ and Λ as follows: $\lambda = (\Lambda/2) \sin(\theta/2)$.

¶The terms "molecule" and "particle" are used as synonyms. Simple liquids are primarily monatomic. In this sense it might be possible to give preference to the word "atom", but it is not completely appropriate in the case of metallic liquids.

If the scattering is coherent, then for a given **k**, integration of $S(\mathbf{k}, \omega)$ with respect to all frequencies gives an expression for the static structure factor:

$$S(\mathbf{k}) = \int_{-\infty}^{\infty} S(\mathbf{k}, \omega)\, d\omega$$

The scattering function $S(k, \omega)$ can be calculated using model representations. A particularly important feature, however, is that $S(k, \omega)$ can be found from neutron scattering experiments.

The dynamic structure factors of liquid argon close to the melting point, 83.8 K, and of sodium at 506 K (m.p. = 370.9 K), are given in Fig.3. In spite of the differences in the nature of the interaction between the particles in sodium and argon, the dynamic characteristics of their structures are of the same type. The spectrum of the density fluctuations of sodium has many more high-frequency modes, however, and the spectrum of argon many more low-frequency modes. It may be noted that with decrease in temperature there is a decrease in the width of the range of values of $S(k, \omega)$ with respect to the variable ω. Thus the dynamic structure factors of liquid sodium and argon approach even closer in the region of the melting point.

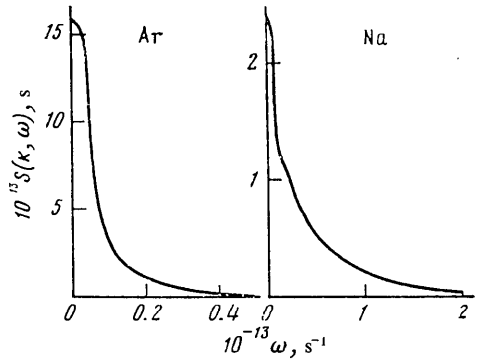


Figure 3. Dynamic structure factor for liquid argon (85.2 K) [16] and for liquid sodium (506 K) [17] with wavenumber $k_1 = 2$ Å^{-1}, corresponding to the position of the first $S(k)$ maximum.

3. The Nature of Thermal Motion in a Liquid

Attention has been drawn to the complexity of the concept of the structure of a simple liquid. To create the correct geometric representation of a structure (this is usually the problem posed), it is necessary to find a method for separating the characteristic indications of the structure from the large number of "transient" configurations arising in the process of thermal motion. This motion has collective and individual components. Ideas about the nature of the thermal motion of individual molecules in a dense liquid have changed with the passage of time. Van der Waals' approach led to the following picture. A particle undergoes hard elastic collisions with the particles of its environment. Between collisions, it moves freely, that is the average field does not change its rate vector significantly; there is no collective component. Some authors also attach importance to "soft" collisions, which are due to the forces of attraction between the particles and which should lead to convolutions in the path of the molecule between two successive hard collisions.

The Frenkel model of a dense liquid[6] assumes another basic mechanism of individual thermal motion: the molecule vibrates about a temporary equilibrium position, and then jumps abruptly to another position, at the foot of the potential well formed by the particles of the new environment. The magnitude of the jumps is close to the average distance between nearest neighbours d. The period of the vibrations τ_0 and the average settled time τ_s are the characteristic time scales in this model of a liquid. Their use together with the parameter d makes it possible to estimate the kinetic coefficients.

The use of molecular-dynamic computer modelling[18-20] has helped to answer questions about the real picture of the thermal motion of the individual particles of a liquid of the argon type close to the triple point, and about the method of study that will make it possible to establish it.

The modelling of simple liquids of the argon type is usually carried out assuming a pairwise central interaction between the particles. The computer is used to calculate numerically the trajectories of the particles with a time step Δt. The results obtained close to the triple point for a model of argon containing in the basic cell 108 interacting (Lennard-Jones potential) particles[21] are given below. The step size in the integration of the equations of motion Δt was 10^{-14} s.

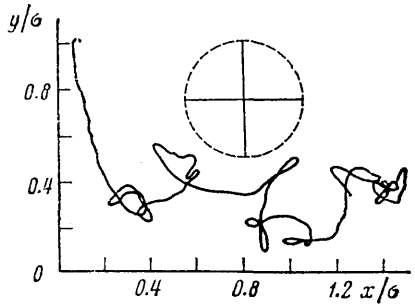


Figure 4. Projection of the trajectory of the motion of a particle on a plane in the molecular-dynamic model of liquid argon[21], 84 K; time interval 10^{-11} s; σ is the effective diameter of the particle (the parameter of the Lennard-Jones potential).

The motion of each particle resembles the Brownian drift in the field of the changing environment (Fig.4). This motion includes a high-frequency component (Fig.5), but it is difficult to distinguish it in the train of approximately monochromatic vibrations about the temporary equilibrium position and in the jump to a new fixed position. The time interval in Fig.4 contains 10^3 steps in the integration of the equations of motion, so that the picture of the individual motion is obtained with a high resolution. The two sections in the circle, intersecting at right angles (Fig.4) show the magnitude of the displacement of the argon atom in a time of 7×10^{-13} s for motion with an average thermal velocity. For a crystal near the triple point, the motion of the particle is concentrated in the region bounded by the broken circle in Fig.4. The maximum of the spectral density $f(\omega)$ of the

auto-correlation function of the velocity of the particle is observed at $\omega' = 2 \times 10^{12}$ s^{-1}, which corresponds to the most probable frequency of the individual vibrations of the atoms in the liquid. If the gas-dynamic approximation is used, a value close to ω' is obtained for the average number of collisions of the particle. Examination of a selected particle together with its environment, and the dynamic structure factor[20,22], shows, however, that the molecular motion in a dense liquid is essentially collective in character.

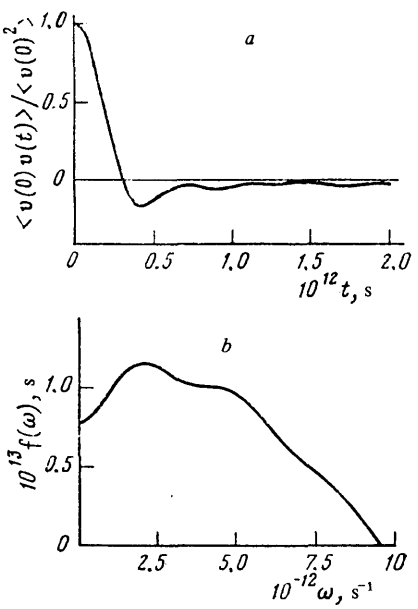


Figure 5. Self-correlation rate function (*a*) and its time Fourier transform (spectral density) (*b*) for the MD model of liquid argon (84 K).[21]

Table 1 gives the characteristic values of quantities related to the static and dynamic structures for two simple liquids, argon and sodium, close to the triple point. Table 1 was compiled using data from Refs.9, 11, 15–17, 21, 22. The average distance between the particles d was obtained as $v^{1/3} = (V/N)^{1/3}$. The positions of the first and second maxima of the RDF give the radii of the first and second coordination spheres r_1 and r_2. The average coordination numbers are determined by the integrals

$$\bar{z}_1 = \int_0^{r_{m1}} d z, \quad \bar{z}_2 = \int_{r_{m1}}^{r_{m2}} d z,$$

where r_{mj} is the position of the jth minimum of the RDF. The local coordination number $\delta z = dz$ is the average number of neighbours in a spherical layer of thickness δr at a distance r from the central particle:

$$\delta z = \frac{4\pi}{v} g(r) r^2 \delta r, \quad \delta r = (r_{i+1} - r_{i-1})/2;$$

the subscript $i = 1, 2, \ldots$ denotes the points of division of the interval in which the RDF was obtained from the experiment. The blurring of the coordination layers is characterised by the second moments of δz_1, δz_2, that is

$$\tilde{\Delta} z = \langle (\delta z - \bar{\delta z})^2 \rangle^{1/2} / \bar{\delta z}$$

The position of the first maximum of $S(k)$ is denoted by k. The average rate of thermal motion $u = (k_B T/m)^{1/2}$, and D is the self-diffusion coefficient. The characteristic frequency of the individual vibrations of the atoms (the position of the principal maximum of the frequency spectrum of the auto-correlation function of the velocity) is denoted ω'. In liquid alkali metals, propagating collective vibrations (modes) with fairly short wavelengths λ are observed (as far as $\lambda \cong 1.5\lambda_1$, where $\lambda_1 = 2\pi/k_1$ is the characteristic wavelength of the order of the interatomic distances). In liquid argon, only modes with $\lambda \geq (5-7)\lambda_1$ can be propagated, but as in liquid sodium, a mode of the relaxation type exists in argon. The characteristic frequency of this excitation ω_c is determined via the half-width of $S(k_1, \omega)$; ω_D is the Debye frequency (it depends on the temperature of the solid for which it is determined), and $\tau_R = \eta/G$ is the Maxwell relaxation time (η is the shear viscosity of the liquid, and the value of the shear modulus G is taken for the solid substance).

Table 1. Space–time characteristics of the structure of liquid argon (m.p. = 83.8 K) and sodium (m.p. = 370.9 K) close to the melting point.

Characteristic	Ar	Na	Characteristic	Ar	Na
T, K	85	373	k_1, Å^{-1}	2.0	2.0
d, Å	4.05	3.76	u, m s^{-1}	133	367
r_1, Å	3.67	3.82	$10^5 D$, cm^2 s^{-1}	1.9	5.8
r_2, Å	6.94	6.9	$10^{-13}\omega'$, s^{-1}	0.2	2.0
$\bar{z}_1$	12.2	13.9	$10^{-13}\omega_c$, s^{-1}	0.06	0.13 (T=506 K)
$\tilde{\Delta} z_1$	0.50	0.54	$10^{-13}\omega_D$, s^{-1}	1.0±0.2	1.5±0.3
$\bar{z}_2$	42.6	45.8	$10^{-13}\tau_R$, s^{-1}	0.3	0.8
$\tilde{\Delta} z_2$	0.40	0.39			

Table 1 shows that the greatest difference is between the principal frequencies of the individual vibrations of the atoms. This is due chiefly to the difference in the strengths of the interactions between the particles in liquid argon and sodium. The Na ions are in a stronger surrounding field than the Ar atoms. Thus the vibrations of the Na ions in this field also take place with a higher frequency than those of the Ar atoms. The characteristics of the static structure of liquid argon and sodium do not differ so markedly.

IV. THE RESULTS OF THE USE OF SIMPLE MODELS

1. Bernal's Model Representations

In the late nineteen-fifties, Bernal[23] stated that the structures of the short-range order in a liquid and in a crystal are essentially different. Bernal pointed out the inadequacy of the quasi-crystalline concept in the theory of simple liquids. He later pointed out[24] the symmetry-related source of this difference: "A necessary geometric property of any lattice or any structure constructed in a lattice, no matter how small its dimensions, is the presence of a definite form of axial symmetry, of second, third, fourth, or sixth order. Symmetry of fifth order is impossible in a crystal lattice, however". In the irregular structure of a liquid, however,

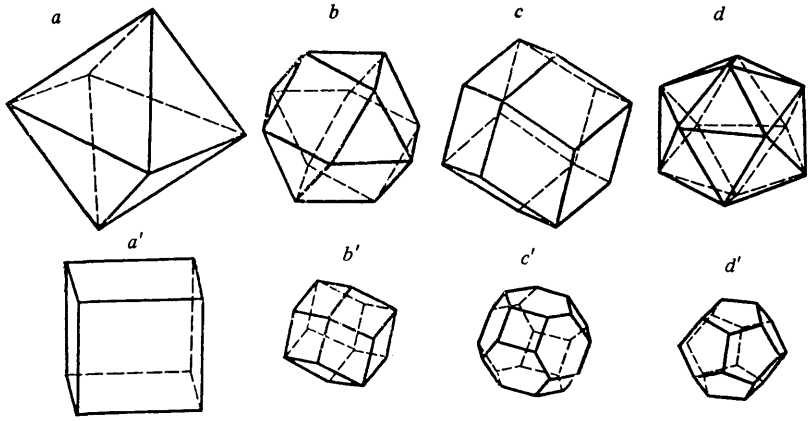


Figure 6. Polyhedra for the nearest neighbours (particles situated at the centre and apices of the polyhedra) in the ideal simple cubic (*a*), face-centred cubic (*b*), and body-centred cubic (*c*) lattices and for icosahedral coordination (*d*). The corresponding Voronoi polyhedra are: cube (*a'*), rhomboidal dodecahedron (*b'*), cubo-octahedron (*c'*), and dodecahedron (*d'*).[21]

other types of symmetry may be found. For example, elements with symmetry of fifth order are characteristic of dense random packing.

Since Bernal was interested in problems of the geometric structure of liquids, he turned to mechanical models, believing that random dense packing is closest to the typical molecular configurations of a simple liquid. Models of different types were used: 1) ball and spoke, 2) wax and plasticine spheres, and 3) steel (non-deformable) spheres. In the first type of model, a random distribution was approached by the successive addition of spokes whose length was selected in accordance with the RDF of argon, or by specifying the coordinates of the centres of the spheres by means of a computer using an established program ensuring a random distribution. The second type of model was subjected to compression, and the spheres were converted into polyhedra (analogues of the Wigner–Seitz cells), whose shape reflected directly the relative arrangement of neighbours. To make the corresponding construction without resorting to deformation of the spheres and replacing them altogether by points, the following procedure was used. Through the centres of the sections connecting the selected point (the centre of the sphere) to the points surrounding it, planes normal to the sections are constructed. The intersection of the planes gives a set of polyhedra round the given point. The convex internal polyhedron, which is not intersected by other planes, is called the Voronoi polyhedron (VP). It reflects the arrangement in space of the points nearest the selected point. The VP is a cube for a simple cubic lattice, a cubo-octahedron for a body-centred cubic lattice, and a rhomboidal dodecahedron for a face-centred cubic lattice. This correspondence between the cell and the VP is shown in Fig.6; to it is added another example—the Voronoi polyhedron for an element of an irregular arrangement of atoms—which can be represented by an icosahedron or by twelve deformed tetrahedra.

Bernal analysed the set of polyhedra obtained in the deformed model. it was found that the average number of faces of the Voronoi polyhedron $\bar{n} = 13.3$ (in the ball and spoke model, $\bar{n} = 13.6$), and of all types of face $3 \leq m \leq 7$ (m is the number of sides of the face), the quadrilateral was encountered most frequently; averaging over all the polyhedra gave $\bar{m} = 4.3$. The existence of five-particle configurations in the model of the liquid (the proportion of pentagonal faces was 27%, whereas the proportion of quadrilateral faces was 48%) is known to exclude the possibility of a regular structure. This characteristic, according to Bernal, reflects a fundamental structural property of a liquid.

The mathematical study of three-dimensional irregular networks[25] gives a higher value $\bar{m} = 5.115$ and a similar value $\bar{n} = 13.56$.

When polyhedra are obtained in close packing by compressing a model, fairly small faces and edges of the polyhedra are revealed ineffectively or not at all. Thus Bernal's analysis does not correspond rigorously to the actual configuration. As shown below, however, the smallest faces apparently should not be taken into account, since they reflect that element of random character which should disappear on appropriate averaging. In the molecular system they arise as the background produced by thermal motion.

Modelling showed that a random close-packed structure is characterised by a certain coordination number distribution function. This was clearly revealed in experiments with steel balls in a balloon[7]. After shaking and compressing the system, paint was poured into the balloon; the paint flowed freely, leaving thicker traces in the form of rings or points at those places on the surface of the spheres where they were in contact or almost in contact with one another. This detected neighbours for which the relative distance between the centres r/σ lay in the range $1 \leq r/\sigma \leq 1.05$.

The next method of studying models of steel balls ($N = 3000$, $\sigma = 6$ mm) was based on the determination of the Cartesian coordinates of each ball using a special measuring device[7]. Similar experiments were carried out by Scott[26] in Toronto. Spheres in a random close-packed structure occupy ~0.64 of the total volume. For a regular close-packed structure, $v_0 N/V = 1/6\pi\sigma^3 N/V = 0.7405$. This corresponds to a ratio of the densities of regular and irregular packing of 1.16. The number obtained is close to the ratio of the densities of crystalline and liquid argon (1.15) close to the triple point. The coordinates of the steel balls measured in

the packing were fed into a computer[27] for the construction and analysis of the Voronoi polyhedra. This gave the values $\bar{n} = 14.28$ and $\bar{m} = 5.16$, which are greater by 5% and 1% respectively than the values of $\bar{n}$ and $\bar{m}$ obtained in Coxeter's theoretical model[25].

The exact construction of the Voronoi polyhedra (with allowance for the small faces and edges) for the model of a simple liquid showed that pentagonal configurations predominate over other arrangements of the spheres. For the steel-ball models, the RDF was constructed and found to show satisfactory agreement with the RDF for liquefied inert gases and alkali metals. The independent determination of the RDF by Bernal and by Scott gave identical results. Thus the model of irregular close packing reflects essential features of the geometric structure of simple liquids. The theoretical study of the hard sphere model (the calculation of the RDF, mentioned above), and also computer modelling[28], lead to the same conclusion. Another conclusion is as follows. The form of the RDF of liquid argon or sodium close to the triple point is not determined by the need for a quasi-crystalline structure of the short-range order. Models show that the RDF arises from a large number of configurations, where there is a predominance of elements of short-range order excluded from the small set of coordinations allowed by the construction of a regular close packed structure.

Bernal also used other geometric methods of studying models. For example, he examined the shapes of the cavities between the spheres, which are clearly revealed in a system constructed from balls and spokes. The cavities (holes), bounded by planes passing (in contrast to the Voronoi polyhedra) through sections connecting nearest neighbours, form a certain set of polyhedra. Their variety is not particularly large, if the examination is restricted to the case where cavities into which a sphere can enter freely are not formed. The random close-packed model is characterised by a much larger number of types of polyhedra than the regular structure, however. In both cases, the predominant form of cavity is the tetrahedron. This reflects a high density of packing, since the tetrahedral coordination of four atoms corresponds to the highest local density (0.7795). A very compact formation is obtained by the connection of several tetrahedra. Bernal called these formations pseudo-nuclei. The prefix "pseudo" is related to the fact that a regular structure cannot be constructed from tetrahedra, but slightly curved chain formations of tetrahedra are possible.

The study of the angular distribution of neighbours in the models revealed the existence of groups of 4–6 atoms arranged almost in straight lines. These randomly oriented "collinear formations", according to Bernal, are a characteristic sign of irregular close packing.

Thus the use of mechanical models has proved extremely valuable in the investigation of a dense irregular structure. The absence of restrictions associated with regularity permits a large number of additional coordinations not characteristic of the crystal, and these configurations predominate. In this approach (for which there is justification) the structure of the short-range order of simple liquids is contrasted with the crystal structure.

2. Clusters with Minimum Energy

In the purely geometric approach to the determination of the structure of liquids, the role of inter-particle interaction and thermal motion is underestimated. In hard sphere models, the impenetrability of the spheres is equivalent to the introduction of repulsive forces (1), but forces of attraction are ignored. The more realistic Lennard-Jones and Morse potentials have been used to determine the optimum structure of clusters from a small number of interacting atoms. The configuration with the minimum potential energy U_{min} was found. For $N = 2$ there is one configuration. With increase in N there is an increase in not only the total number of configurations but also the number of relatively stable forms. Even for $N > 4$, the search for the spatial arrangement of the particles corresponding to the absolute minimum energy becomes difficult. Fig.7 shows the sequence of optimum figures for clusters containing up to 13 atoms[29].

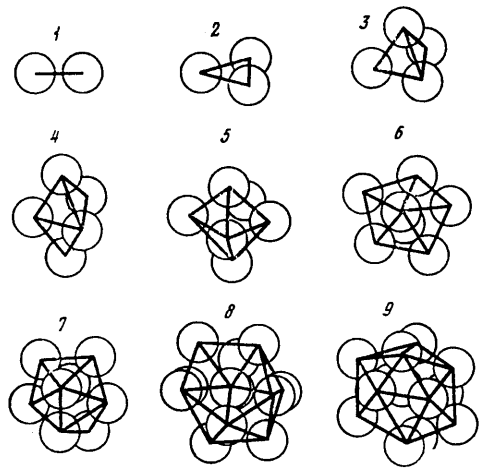


Figure 7. Sequence of small clusters with optimum shape: *1*) dimer (*2*), *2*) equilateral triangle (*3*), *3*) tetrahedron (*4*), *4*) twinned tetrahedra (*5*), *5*) octahedron (*6*), *6*) pentagonal bipyramid (*7*), *7*) bipyramid *6* brought up to eight atoms (*8*), *8*) bipyramid *6* brought up to 12 atoms (*12*), *9*) icosahedron (*13*); the number of atoms in the sequence is given in parentheses.

Most stable configurations are of the non-crystalline type, that is they cannot be elements of a regular lattice; they may, however, be present in an irregular structure of the liquid type. In this sense, the study of clusters with a free surface is also of interest for the investigation of the structure of liquids.

The use of modern fast computers makes it possible to increase the number of optimum figures to values $N > 13$. The examination of a given sequence of configurations is partly replaced by restricted or even free relaxation of the system. For example, a published algorithm[30] provides for the motion of each atom in the direction of the acting force in steps whose length is proportional to the magnitude of the force.

The initial configuration of the model of a cluster containing several tens of particles can be selected in accordance with the packing of tetrahedra[31], which determines the variety of forms of a cluster and its symmetry. In spite of the fact that the tetrahedron is an element of a regular (face-centred cubic) structure (together with the octahedron), it is impossible to fill an appreciable proportion of space by tetrahedra alone in compact form (without cavities). Twenty tetrahedra, combined in a convex compact figure (the centre of the figure is a common apex of the tetrahedra) form a

minimum of eleven pairs of non-contacting planes, giving gaps of different volume. If these gaps did not exist, that is if all the faces of the tetrahedra touched, an icosahedron would be obtained. For this to happen, however, it is necessary to deform the tetrahedra by reducing all the distances from the centre of the figure to its apices by a factor of ~1.048, leaving the distances between adjacent external angles unchanged.

It is assumed that atoms are situated at the centre of the figure and the apices (existing and assumed) through which a five-fold axis of symmetry passes. If this 13-atom cluster is allowed to change its configuration ($U \to U_{min}$), the result of relaxation will be an arrangement of atoms corresponding to an icosahedron. Seventeen tetrahedra, combined in definite fashion[31], after structural relaxation form a cluster of fourteen atoms with the symmetry of the tetrahedron (four three-fold axes of rotation). The same symmetry is shown by 26- and 38-atom clusters. A cluster formed by the packing of tetrahedra can also have the complete (33 atoms) and partial (45 atoms) symmetry of the dodecahedron, that is twelve five-fold axes of symmetry. High symmetry, however, does not guarantee an increased stability of the cluster. In a cluster containing $N < 50$ atoms, an arrangement of particles obtained from the packing of tetrahedra is more favourable than face-centred cubic or hexagonal close packing. The stability of clusters of large dimensions depends markedly on the form of the interaction potential responsible for the structural relaxation. The estimation of the equilibrium form of the cluster is made difficult by the fact that for short-range potentials (of the Lennard-Jones type), the main contribution to the energy is made by the first two layers of neighbours, and the difference in the contributions between the third and higher-lying layers is small.

The icosahedron is a structural formation with minimum energy among clusters of the same size (N). A cluster with icosahedral packing may have not only 13 atoms but also 55, 147, 309, 561, ... particles.. When the struture is optimised using a computer, icosahedral symmetry is apparently preserved in subsequent ($N > 561$) clusters for a long-range potential (of the Morse type). In the case of the Lennard-Jones potential, this symmetry may disappear. The symmetry of the icosahedron does not allow it to be the unit cell in a periodic lattice. The icosahedron is used as the basic structural unit in models of dense irregular extended phases such as amorphous metals[32].

In the construction of large clusters, the method of combination is sometimes used[33]. An example of a cluster constructed in this way is the 485-atom dodecahedron obtained by the structural relaxation of a 55-atom icosahedron surrounded by twenty 26-atom clusters with tetrahedral packing. Subsequent "additions" to the cluster brings its "size" up to 4000 atoms.

Increase in the size of the cluster is accompanied by a definite structural rearrangement, which wipes out the differences between its physical properties and those of an extended phase, determined by the high value of the ratio of the surface energies for the cluster and the volume. These differences concern chiefly the nature of the close packing of small groups (clusters) and the changes in their thermophysical properties. The particles of noble metals (dimensions 30–150 Å, that is $N \sim 10^4$–10^6) have been studied by electron microscopy and electron diffraction[34]. The clusters on nucleation had icosahedral packing, but subsequently their structure changed so that the electron diffraction pattern showed a similarity to the face-centred cubic structure. Metallic particles with shapes close to both icosahedral and dodecahedral were observed, possibly due to repeated twinning. The melting point and the Debye temperature for the small particles were lower than for the massive material[35]. The vibrations of the surface atoms in the cluster take place with a larger amplitude and a lower frequency than the vibrations of the atoms in the bulk. This is responsible for the change in the vibrational spectrum and the increase (relative to the massive specimen) in the heat capacity of the cluster.

Molecular-dynamic modelling of the structure of clusters of Ar, Kr, and Xe,[36] formed by 4, 7, and 16 layers of neighbours round a central atom (face-centred cubic lattice) established that in the smallest of these clusters (55 atoms), even at $T \cong 0.16$ m.p.* (m.p.* is the melting point of the cluster), a structural phase transformation takes place, leading to the structure of an icosahedron. Larger clusters (135 and 429 atoms), however, retained the face-centred structure as far as the melting point. The limiting size of a cluster with a structure having stable pentagonal symmetry is not yet known even for the simplest potentials, since this requires the determination of the free energy of a very large number of isomers.

3. Phase Transformations of the Fusion Type in the Hard Sphere Model

In the theory of the liquid state, the view has developed that the hard sphere model reflects the most important features of a dense irregular structure[37]. The chief advantage of the model is its simplicity: the spherical symmetry of the molecules, hard collisions, and free motion between collisions. In a system of hard spheres, the pressure p and the temperature T are proportional to the sum of the squares of the velocities of the spheres, averaged with respect to time or with respect to the ensemble, that is for a given density of packing, the ratio p/T remains constant for any finite values of the velocities. In other words, for the hard sphere model, all the isotherms on coordinates $p/T-V$ are equivalent.

The hard sphere model is widely used in the solution of the integral equations of statistical theory. Here, however, it either does not describe the phase transformation or predicts a disordering transition at densities not corresponding to the real densities. A phase transformation of the fusion type for the hard sphere model was detected in a computer experiment[38]. Computer calculations[39,40] showed that this transformation also exists for a two-dimensional model, that is for a hard disc model. Calculations for a cellular model of the crystal were carried out by the Monte Carlo method[41]. Identical cells filled compactly the space occupied by the particles. The centres of the cells coincided with the sites of the ideal crystal lattice. The cell represented a rhomboidal dodecahedron in the three-dimensional model, and an equilateral hexagon in the planar case. The condition of constant occupancy of the cells was used, that is it was assumed that in the motion of each particle, its centre did not go beyond the limit of the cell assigned to it. A break on the isotherm, indicating a phase transformation, is observed only when the region of the transformation is approached from the direction of the solid (see Fig.8). In the compression of a liquid consisting of hard spheres, a phase transformation was not observed either in computer calculations or when Pade's approximation[41] or Woodcock's equation[42] were used.

In a Monte Carlo experiment, Hoover and Ree[43] located a transition, which they interpreted as fusion, in a system of hard spheres by equating the chemical potentials of the liquid and crystalline phases (the line ab in Fig.8). The

sections of the isotherm *af* and *bc* correspond to metastable states: the supercompressed liquid and the stretched crystal. Table 2 gives the densities found in this way for the liquid and crystalline phases (their ratios to the density of close packing), the values of the pressure and the entropy changes on fusion, and also the corresponding values obtained in the self-consistent cellular model using a cluster expansion[44], and the experimental parameters of the fusion of argon[45] at $p = 1324$ MPa and $T = 295.7$ K. It is assumed that for these values of p and T, the Ar atoms can be described by hard spheres with diameter $\sigma = 3.405$ Å, that is compression leads to changes only in the distances between the atoms, and the size of the atoms themselves remains constant. Soft interaction between the atoms is replaced by hard interaction, and forces of attraction are neglected. It can be seen that the experimental values of $\Delta\rho$ and ΔS for Ar show much better agreement with those calculated by the Monte Carlo method than with those calculated using the self-consistent cellular model. The exponent of the repulsive potential[46] has a strong influence on the change in entropy, free energy (ΔF), and internal energy (ΔU) on fusion, but has little influence on the Lindemann fusion parameter. Thus with change in the exponent of the potential from 4 to ∞ (hard spheres), the values of ΔF increased by a factor of 2.5, whereas the value of $\langle[r(t) - r(0)]^2\rangle^{1/2}$ decreased by not more than 20%.

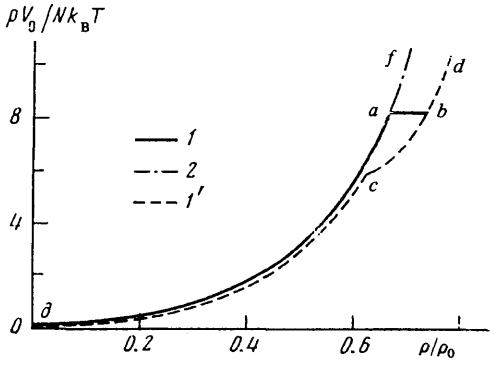


Figure 8. Isotherms for the liquid *ef* (*ec*) and the crystal *cd* in the hard sphere model: *1*) calculation by the Monte Carlo method[41] and using the Pade approximation[41]; *2'*) calculation using the equation of Ref. 42; *1'*) MC calculation in the cellular model[41], the line *ab* corresponds to equality of the chemical potentials of the liquid and solid phases; $V_0 = N\sigma^3\sqrt{2}/2$ is the volume of the close packing.

Table 2. Fusion parameters of hard sphere models and experimental fusion data for crystalline argon at a pressure of 1324 MPa.

Parameter	Monte Carlo method (Refs. 43, 46)	Self-consistent cellular model (Ref. 44)	Experiment (Ref. 45)
ρ_{cr}/ρ_0	0.736±0.003	0.747	0.851
ρ_l/ρ_0	0.667±0.003	0.650	0.805
$\Delta\rho/\rho_0$	0.069	0.097	0.046
pV_0/Nk_BT	8.27±0.13	8.84	9.05
$\Delta S/Nk_B$	1.16	1.77	1.05

The absence of attractive forces and soft interaction makes it possible to regard the disordering transformation in a system of hard spheres (or discs) from purely geometric viewpoints. This can be done most simply for the planar model (in the one-dimensional case, a transition of type I is not observed). In the computer modelling of a system of hard discs, a transformation of the fusion type takes place at the same density of packing as in the static model, when fusion is related[47] to the slipping of a number of discs relative to one another. The same mechanism of fusion is proposed for the three-dimensional model.

V. THE STUDY OF THE STRUCTURE OF A LIQUID BY MOLECULAR-DYNAMIC MODELLING

1. Molecular-Dynamic Modelling Using the Computer

Computer experiments by Monte Carlo (MC) and molecular dynamics (MD) methods have an important place in the study of condensed states of matter. The MC method is generally used to calculate the equilibrium (with averaging with respect to the assembly) properties of a substance, whereas the MD method (averaging carried out with respect to time) can also be used to determine kinetic characteristics (coefficient of self-diffusion, viscosity, thermal conductivity, etc.). Moreover, in the detailed study of the structure of a substance, the MD method has an undoubted advantage over the MC method, in that the configurations of the particles obtained with time are closer to the real values than those obtained by random rearranging of the particles. In this section, particular attention will be paid to the problem of a dense liquid and the crystal⇌liquid phase transformation, that is the range of states for which a theoretical description is difficult.

The MD method is based on the determination of the trajectories of the motion of the particles in the model by numerical integration of the equations of motion. The most widely encountered numerical methods for solving the equations of motion using a computer is the method of prediction and correction[18]. To obtain sufficient accuracy and a satisfactory speed of calculation, two iterations are usually carried out for the accelerations, momenta, and coordinates of the particles. The reliability of the results obtained is controlled from the value of the internal energy U, which should remain constant (in practice, a change in U by ~1% after 10000 time steps is permissible). The principal cell of the three-dimensional model is generally cubic, and contains from several tens to several hundreds (sometimes thousands) of particles. In the study of the properties of a liquid close to the crystallisation range, the number of particles N in the basic cell is selected in accordance with the number of sites of the lattice included in it, which reflects the average positions of the particles in the crystal. For the face-centred cubic lattice, it is assumed that $N = 4n^3$, where $n = 2, 3, 4, 5, 6, \ldots$, that is $N = 32, 108, 256, 500, 864$, etc. In the case of the body-centred cubic lattice, $N = 2n^3$. For the initial arrangement of the particles in the cell when modelling a liquid, either their random distribution or their arrangement at the sites of a given lattice is selected. The direction and magnitude of the initial velocity of the particles is given by a set of random numbers. The absolute values of the velocities for all the particles are corrected in accordance with the selected temperature.

The properties of the macroscopic phase are calculated by applying to the cell periodic boundary conditions to decrease the surface effects due to the small size of the system. By means of the periodic boundary conditions, the main cell is

surrounded by translationally symmetric images (at least 26 of the same cells). The constancy of the particles in the cell is preserved by the periodic boundary conditions; when a particle goes beyond the limits of the cell through one face, an anlogous particle appears in the cell through the opposite face. The interaction of the particles in the model of liquefied inert gases is more frequently described by an effective paired potential $\Phi(r)$ of the Lennard-Jones type. To keep the energy constant, the mutual penetration of the particles is restricted. Usually, the shortest distance r_{min} to which the particles can approach is selected from the condition: $\Phi(r_{min}) \cong 40 k_B T_T$, where T_T is the temperature of the triple point. This gave the value $r_{min} \cong 0.822\sigma$ for argon[18].

At distances greater than ~2.5σ, the interaction between the particles becomes very weak, $\Phi(r)$ amounts to less than 2% of the depth of the potential well, and the direct calculation of the interaction energy is replaced by the introduction of a constant correction determined by the static environment. The correction for a liquid is calculated in the approximation of a uniform distribution of the particles of the periphery, and for a crystal the arrangement of the particles at the sites of an ideal lattice is adopted. The main inaccuracy in the modelling is due[18] to the lack of correspondence between the potential of the interaction between the particles, used in the calculations, and the potential describing the interaction in a real substance. For the Lennard-Jones potential, a time step $\Delta t = 10^{-14}$ s ensures the required accuracy of the calculation of the trajectories for the motion of the particles. For high values of Δt, strong overlap of the volumes of the particles is possible, leading to a change in energy in the system.

The evolution of a system takes place according to the laws of motion of classical mechanics. Usually, in a time interval corresponding to several hundred time steps, a distribution of the particle velocities close to the Maxwellian is established, and the internal energy of the system remains constant with time, that is, the system reaches internal equilibrium. From this moment it is possible to proceed to the calculation of the thermodynamic, structural, and also kinetic properties of the substance being modelled.

Fusion in the three-dimensional model of Lennard-Jones particles has been studied in considerable detail by many authors (see, for example, Refs.20, 48, 49). Similar melting points were established[20] for the MD model and in actual crystalline argon (m.p. $\cong$ 84 K, $p \cong 0.1$ MPa). The complex mechanism of fusion is still not fully understood, however. Analysis of the results of MD calculations from any single viewpoint not only does not clarify but sometimes on the contrary confuses the picture of the real phenomenon.

Cotterill and co-workers[48] studied the mechanism of disordering on the basis of the assumption that spontaneous formation of extended defect-dislocations takes place in the crystal. Although considerable progress has been made in this field (for example, the change in volume on fusion for Ar and Kr crystals was ~15%, in good agreement with the experimental data), nevertheless the dislocation interpretation of fusion must be approached with some care. The description of fusion in this approach is based exclusively on the properties of the ordered phase; the unique nature of the structure of the liquid is ignored. Melikhov and co-workers[49] studied the breakdown of a crystal† within the framework of the cluster model of a liquid. The clusters in the MD model were determined via a correlation function of the distances, which can be calculated in the approximation of the Frenkel mechanism of the motion of the atoms[6] in the solid and liquid phases. The mechanism, convenient for theoretical models, of the motion of the atoms in a liquid as vibrations about equilibrium positions and jumps into new equilibrium positions was not confirmed by MD modelling[20]. The conclusions reached[49] appear doubtful, however. Thus it is assumed[49] that fusion is due to the production of the nuclei of an irregular structure, and that the critical nucleus should contain one or two particles. The concept of "structure" (in its geometric sense) clearly has no meaning for such small "formations".

It has been shown[50,51] that the breakdown of the lattice of a face-centred cubic crystal is due primarily to displacements of the particles in a close-packed plane; a body-centred cubic crystal with a Lennard-Jones interaction of the particles is also unstable with respect to displacements in the most highly pupulated plane, which is the (110) plane (in contrast to the (111) plane for the face-centred cubic crystal).

2. The Crystallisation and Stability of a Supercooled Liquid

In recent years, considerable effort has been directed to the study of the crystallisation of a supercooled liquid by MD modelling. Rahman and co-workers[52-55] studied processes of vitrification and crystallisation in Lennard-Jones systems. The vitreous state of argon was obtained[52] in a system of 500 particles, and the transition to the glass was studied in more detail for a system of 108 particles. The radial distribution function $g(r)$ of vitreous argon (see Fig.9) has a clearly defined double peak with maxima at $r/\sigma \cong \sqrt{3}$ and 2, indicating random close packing of the particles in the system. A simple explanation has been proposed[56] for the production of these peaks, using the concepts of contacts between hard spheres. Thus the peak at $r/\sigma \cong 2$ is due to contacts between spheres with a gap which does not allow them to approach more closely. The peak at $r/\sigma \cong \sqrt{3}$ is observed for the contacts of four hard spheres when the two equilateral triangles which they form have a common edge, around which they are able to rotate through an angle which defines the blurring of the peak. Close to the triple point for a face-centred cubic crystal or argon, the maxima of the second and third peaks of $g(r)$ correspond to values $r/\sigma \cong 1.6$ and 2, and for the liquid, $g(r)$ has a second peak which is not split, with a maximum at $r/\sigma \cong 2$. The splitting of the second peak of $g(r)$ on the vitrification of argon (broken line in Fig.9) begins at $T \cong 50$ K ($p = 8.6$ MPa).

In spite of the satisfactory approximation of the RDF of vitreous argon within two coordination spheres by the function $g(r)$ for a body-centred cubic crystal with Lennard-Jones interaction of the particles, the microstructures of these states are different[57]. The shear viscosity of vitreous argon[52], determined from the Einstein–Stokes relationship (via the calculated coefficient of self-diffusion $D = 10^{-9}$ cm^2 s^{-1}) is ~100 Pa.s. This value is ~37 times the viscosity of liquid argon close to the triple point.

The crystallisation process has been studied[53-55] for systems of 108, 256, and 500 Lennard-Jones particles. From the value of $S(k)$ at different points in the space occupied by the particles, it was found that the critical nucleus should contain ~40–70 particles. The type of nucleating strongly-defect crystal structure depends on the nature of the interaction between the particles. In a model of 500 particles of supercooled rubidium (shielding by electrons was taken into account in the potential), the transition to a body-centred cubic crystal was detected[55]. After crystallisation, the

†In fact, Melikhov and co-workers[49] studied not the fusion but the spinodal breakdown of an argon crystal superheated by a factor of 2.86 relative to the melting point ($p \cong 105$ MPa).

potential for rubidium was replaced by a short-range potential (only the repulsive branch of the potential for rubidium, the Lennard-Jones potential, and its repulsive part were used), as a result of which the structure relaxed into the face-centred cubic lattice.

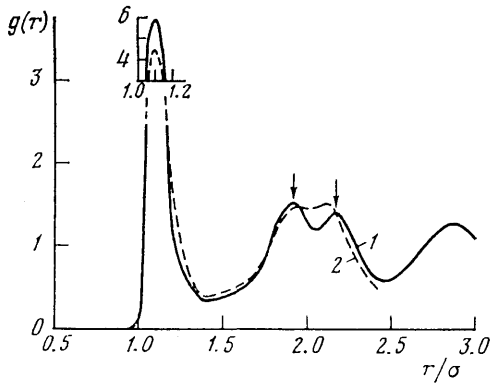


Figure 9. Radial distribution function of vitreous argon, obtained in the MD model: *1*) $T = 12.9$ K, $\rho = 1.596$ g cm^{-3},[52] the arrows indicate the positions of the two maxima of the split peak at $r/\sigma = 1.93$ and 2.16; *2*) $T = 48.8$ K, $\rho = 1.667$ g cm^{-3}.[57]

The actual identification of the crystalline nucleus presents considerable difficulty in the MD experiment. It has been suggested[58] that in MD modelling, the following factors have a decisive influence on the production of a regular structure: 1) the error of the method of integrating the equations of motion; 2) the rounding-off error of the computer calculation; and 3) the periodic boundary conditions. In the MD models, however, crystallisation was observed for different (including short-range) potentials of intermolecular interaction, so that the errors in the integration and the application of the periodic boundary conditions can hardly play a decisive role, since these errors have a smaller order of smallness than the perturbations associated with a change in the potential.

The computer experiments[53–55] may have detected not genuine crystallisation but a preceding stage of heterogeneous fluctuations in the supercooled system in which an ensemble of prenucleation formations is produced and relaxes to the stationary state.

Schneider and co-workers[59] proposed to study the possibility of another mechanism of crystallisation. It is assumed that a supercooled liquid may be unstable with respect to perturbations of the density, taking place throughout the volume of the liquid and having a wavelength of the order of the interatomic distances. Schneider's hypothesis was verified[60,61] in a study of a Lennard-Jones liquid with respect to external time-independent perturbations. In both the planar[60] and the three-dimensional[61] cases, when a periodic perturbing potential was applied, ordering of the particles in the model was obtained. As soon as the potential was removed, however, the system returned to the internal-equilibrium liquid state.

The response of a system to an external perturbation is closely related to the fluctuations in the density, taking place in the system itself (fluctuation–dissociation theorem). Thus the reaction of a system to external perturbations can be found via the calculated spectrum of the density fluctuations. A criterion of the thermodynamic stability of the isotropic phase (in the long-wave limit) is the fulfilment of the inequality[62,63]:

$$T/C_p > 0, \quad -(\partial p/\partial V)_T = (V\beta_T)^{-1} > 0$$

According to Schneider[59], in the static case the system will be stable with respect to perturbations of arbitrary wavelength with the condition

$$\beta_T^{-1}(\mathbf{k}) = \rho k_B T/S(\mathbf{k}) > 0 \qquad (5)$$

Here, $\beta_T(\mathbf{k})$ is the isothermal response function for a time-independent perturbation.

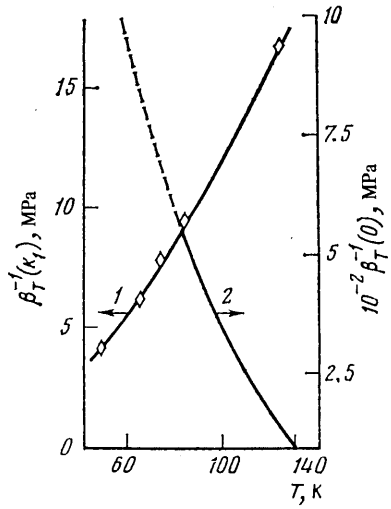


Figure 10. Elasticity of the liquid with respect to long-wave ($\beta_T^{-1}(0) \equiv \beta_T^{-1}$) and short-wave [$\beta_T^{-1}(k_1)$] perturbations: *1*) result of molecular-dynamic calculation[22], *2*) experiment[64]; the broken line corresponds to the extrapolation of the experimental data.

The elasticity of a simple liquid towards short-wave perturbations decreases with decrease in temperature, whereas the thermodynamic (long-wave) elasticity increases (see Fig. 10).[22] In the temperature range studied (with a deep descent into the metastable range), condition (5) is fulfilled both for $k = 0$ and for $k = k_1$. The increase in the mechanical stability to long-wave perturbations ($\beta_T^{-1}(0)$ increases), together with the fulfilment of the thermal stability condition $T/C_p > 0$,[21] indicates the absence of a boundary of appreciable instability (spinodal for the supercooled liquid). Attention was first drawn to this fact by Skripov and Baidakov[65]. The essential feature of this statement is that if the treatment is restricted to an examination of small (continuous) perturbations of the type of fluctuations in the density and energy, the liquid retains its internal stability to as low a temperature as desired. In a real experiment, breakdown of stability may take place as a result of the spontaneous production of a crystalline nucleus (a perturbation of special form) or as a consequence of dynamic instability.

To detect the dynamic (phonon) instability of a liquid, it is necessary to determine the temperature dependence of the dynamic structure factor $S(k, \omega)$ in the deep descent to the range of metastable states. If with change in the thermodynamic state of a system the complex frequency of any collective vibration decreases to zero (soft mode), the system approaches the limit of stability[66]. The frequency of the collective mode Γ_c [half-width $S(k, \omega)$], determined in the MD model of argon[22], decreases more rapidly with temperature than Γ_c calculated in the central field approximation[67] or the generalised Pathak–Singwi approximation[68] (Fig.11). The explicit form of the $\Gamma_c(T)$ relationship was obtained in the form of a polynomial of second degree on treatment of the results of the MD calculation by the least-squares method

$$\Gamma_c(T) = -2.36 + 0.045T - 0.00012T^2 \qquad (6)$$

(in units of 10^{12} s^{-1}). The $\Gamma_c(T)$ relationship in the form of Eqn.(6) is given by the broken line in Fig.11. At $T \cong 64$ K, the polynomial in Eqn.(6) becomes zero. This result, however, apparently cannot be interpreted as the attainment of the limit of dynamic stability of the simple liquid ($k \cong k_1$). At low temperatures ($T < 65$ K for Ar), vitrification of the supercooled liquid takes place, accompanied by a marked increase in the relaxation time. This leads to a no less marked decrease in the half-width of the first (quasi-elastic) peak for $S(k, \omega)$, compared with that for the change to crystalline order. The instability of the liquid can be judged from the decrease in Γ_c when it is certain that the decrease in Γ_c is not due to some other factor.

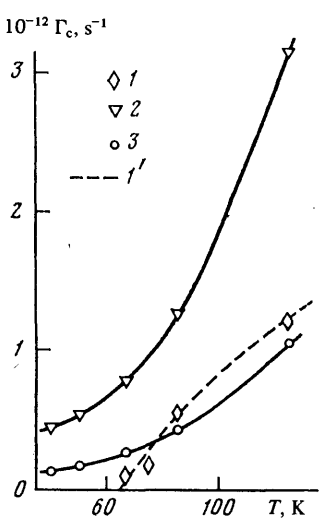


Figure 11. Temperature dependence of the frequency of the collective mode Γ_c: *1*) data from a computer experiment[22], *1'*) result of the approximation of $\Gamma_c(T)$ by the polynomial *6*; *2*) central field approximation[67]; *3*) Pathak–Singwi approximation[68].

The above examination was restricted to simple liquids. For substances with complex molecules, in the description of the structure of the condensed phases, it is necessary to take into account the orientational effects and internal degrees of freedom. The latter influence the "external" dynamics of the system as a consequence of the exchange of energy between different degrees of freedom[69].

3. The Method of Statistical Geometry (Developed for the Computer)

Statistical geometry involves the analysis of the geometric elements characterising the packing of the atoms, based on the construction of Voronoi polyhedra (the Dirichlet region) or Delaunay tetrahedra. The definition and method of construction of the Voronoi polyhedra (VP) were given above in the description of Bernal's mechanical models. Another method of breaking down the space occupied by the particles is associated with the name of Delaunay and is based on the construction of irregular tetrahedra (IT) or, more accurately, triangular pyramids. The method used by Bernal to study the structure of simple liquids by examining the shapes of the cavities formed by the particles reduces to the Delaunay-tetrahedra method. The apices of the IT coincide with the centres of four closely situated particles. For the case of the packing of hard spheres, the IT combines both spheres in direct contact with one another and spheres separated by a small gap (see Fig.12). The section connecting the centres of two spheres in contact is called an edge of the IT,[70] and the section connecting spheres not in contact is called a diagonal of the IT. Each additional particle placed inside the IT leads to the appearance of four smaller IT. For an ensemble of randomly close-packed hard spheres of equal size, the probability of the appearance of a new edge of the IT is 3/4, and that for a diagonal is 1/4. Any IT can be represented by a Delaunay diagram, which describes the nature of the contact between the particles forming it. For a random arrangement of the particles, it is possible to calculate the frequency of the appearance of a given type of IT.

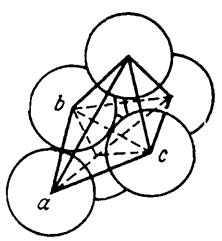


Figure 12. Delaunay tetrahedra for the packing of hard spheres: *ab*—edge of the IT, *ac*—diagonal of the IT.

This method of examination is convenient for the description of the packing of particles of different size, since the distance between the particles is itself an object of statistical analysis. For the study of the regular features of the packing of particles of equal size, however, the method based on the construction of the VP has been more widely used. The methods of describing the structure of the packing of particles on the basis of the VP and the IT are closely related. Thus the number of faces of the VP is determined by the sum of all edges and diagonals passing through an apex "common" to a group of IT (with allowance for all

acceptable versions of the breakdown of space into IT). In a structural analysis using the computer, the VP method is more convenient than the IT method, in that it relates to one definite particle and characterises its environment; the VP carries information on the number and relative arrangement of the nearest geometric neighbours.

Various exact and approximate methods for the computer construction of the VP exist[71-75]. The method proposed by Galashev[75] can be described as follows. The configuration of the system of particles, obtained in the MD experiment for a given step, was known; VP were constructed around the centres of individual particles in the model. Intersecting planes were constructed for the particle environment selected round the centre being considered. From the centre O, a sphere of radius OM was drawn at half the distance to the nearest neighbour; ~200 points were arranged uniformly over the sphere. The points M_c at which the rays, starting at the centre, which had passed through the points arranged on the sphere, meet the set of intersecting planes were then found (see Fig.13). The planes nearest the centre formed the VP. The number of points used ensured that account was taken of all the faces and edges of the VP with area $s > 0.01\bar{s}$ and length $l > 0.1\bar{l}$ respectively, where $\bar{s}$ is the average area of a face, and $\bar{l}$ the average length of an edge of the VP. The accuracy of the construction of the VP can be made as high as desired, by increasing the number of reference points (nodes of the net).

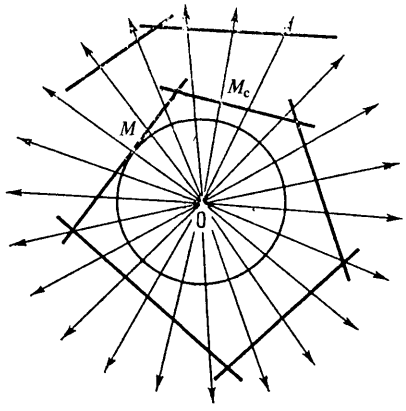


Figure 13. Construction of the VP and its faces by an approximate method[75] (projection of three-dimensional specimens on a plane): *OM* is the radius of a sphere equal to half the distance to the nearest neighbour; the straight lines represent planes passing at right angles through the centres of sections joining the central particle *O* to its neighbours; the arrows leaving the point *O* are the rays; M_c represents the points where the rays meet the planes. The construction used to determine the faces of the VP has a similar form.

The study of the structure of a simple liquid by the method of statistical geometry using a computer led to the discovery of a number of interesting regular features. Thus Rahman[19] established that the average number of geometric neighbours (or the number of faces in the polyhedra) in a simple liquid increases according to a linear law with change in the order of the layer of neighbours from one to five. The magnitude of the calculated average displacement vector, determined as the sum of the vectors drawn from the centre to the apices of the VP, coincides with that of the displacement of the central particle in a time of $\sim 5 \times 10^{-13}$ s. Finney[76] studied the types of VP encountered for a simple liquid in the mechanical hard sphere model and for modelling by the MC method[10]. The predominant VP in the liquid had a relatively simple form, containing, for example, only four-, five-, and six-sided faces.

Statistical geometry was recently used to study the nucleation of a crystalline phase. The states were identified beforehand from the topological characteristics of the VP. The configurations of 108 and 500 particles, averaged over a time interval of 5×10^{-13} s, were analysed[77]. For the model of a liquid with only repulsive interaction (exponent 12), the number of VP having a set of four-, five-, and six-sided faces for a total number of faces of 13 or 14 reached ~5% of the total number of VP (see Fig.14). Fig.14 also shows that for a supercooled liquid the picture is almost identical, although the number of definite groups of 13- or 14-faced VP having only four-, five-, and six-sided faces is close to 10%. In a face-centred cubic crystal, the fraction of characteristic types of VP amounted to up to 20%. For the body-centred cubic crystal, more than 90% of all the VP belong to the class of the cubo-octahedron. The difference in the number of VP of characteristic type for regular packing is due to the fact that the cubo-octahedron (see Fig.6*c'*) is stable with respect to thermal vibrations of the particles, whereas the rhomboidal dodecahedron (Fig.6*b'*) is completely unstable to these displacements[55].

The initial stage of crystallisation has been studied. In a supercooled liquid, discrete "nuclei" combining several particles were detected; the VP of these groups belonged to the class of the cubo-octahedron. With the passage of time, the nuclei grew to form a large particle of irregular shape, containing several tens of atoms with a distorted body-centred cubic structure. When uniform compression of the system was applied along a definite axis[78] (the degree of compression was varied from 0.90 to 0.71), structural relaxation to the face-centred cubic structure took place in it after ~2000 time steps. Hsu and Rahman[55,79] consider, on the basis of the MD experiment carried out, that the crystallisation of liquid argon begins with the simultaneous formation of face-centred cubic and hexagonal close-packed structures, whereas for rubidium the body-centred cubic lattice is formed.

Up to the present, only the positive features of the method of structural analysis based on the VP have been noted. This method, however, has a serious disadvantage. The statistics (frequencies of appearance) of the faces and edges of the VP are essentially topological, and not metric characteristics. It is therefore sometimes difficult to interpret the results of the analysis of the VP. Thus the distortions of the VP brought about by the thermal vibrations of the particles do not make it possible to identify the face-centred cubic structure reliably. Finney and Wallace[80] studied the structure of non-crystalline close packing using a characteristic which is very sensitive to both topological and metric changes—the correlation function for the cavities formed by the particles. They examined two types of cavity[80], a distorted tetrahedron and a distorted octahedron, and concluded that other types of Bernal cavity are rarely encountered in systems with soft interaction, because of the existence of a relatively large (compared with the packing of hard spheres) free volume corresponding to one particle.

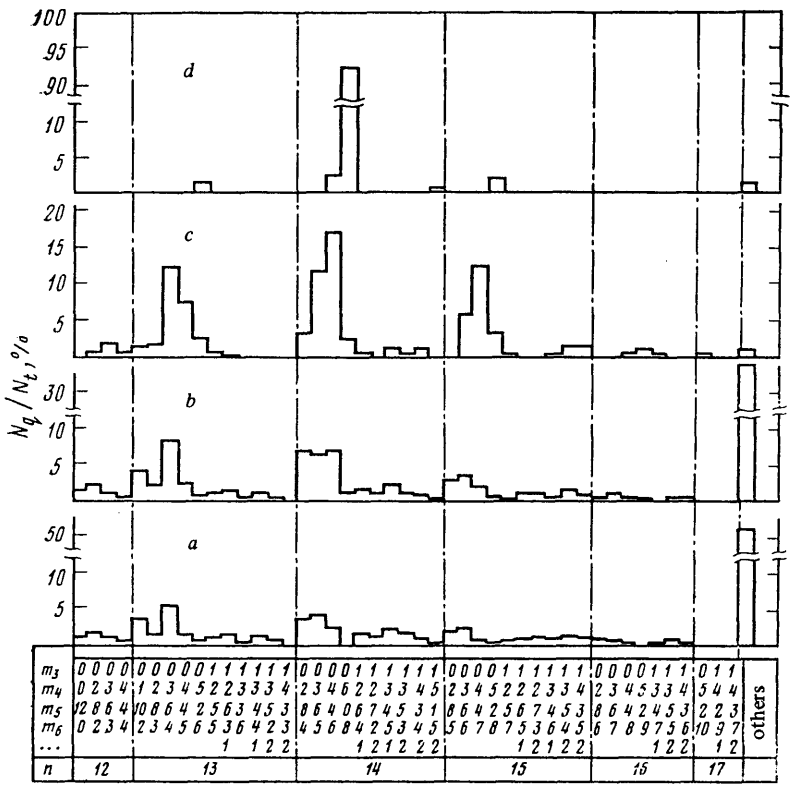


Figure 14. Distribution of the types of VP encountered in the MD models of systems with purely repulsion interaction of the particles[77]; $\Sigma m_i = n$, m_i is the number of i-sided faces in the VP with n faces; N_q/N_t is the relative number of VP containing n faces with i sides; *a*) equilibrium liquid (T = 96.2 K, ρ = 1.511 g cm^{-3}); *b*) supercooled liquid (T = 52.9 K, ρ = 1.847 g cm^{-3}); *c*) face-centred cubic crystal (T = 57.7 K, ρ = 2.099 g cm^{-3}); *d*) body-centred cubic crystal (T = 56.2 K, ρ = 2.099 g cm^{-3}); the values of T and ρ, given in brackets, were calculated for the parameters of the interaction potential σ and ε corresponding to argon.

4. The Structures of the Short-Range Order of the Crystal and the Liquid (the Argon Model)

The short-range coordination of atoms in a liquid has been established from experiments on the diffraction of electrons, neutrons, and X-rays. This coordination does not reduce to crystalline coordination, and is produced by a much larger set of configurations of neighbours. The studies of Bernal, devoted to the investigation of the variety of structures in simple liquids, were discussed above. At the present time, in addition to the alternative approach[7,24], ordering in a liquid is still being interpreted as quasi-crystalline. Use is made, for example, of the models of blurred lattices[81] and floating microcrystallites[82], cluster models in the form of sets of body-centred cubic and face-centred cubic structures[83], etc. The view[84], based on the concept of the quasi-crystallinity of a liquid, that polymorphism exists in liquid metals, is widely encountered. These views are based on an *a priori* under-estimation of the difference between the liquid and the crystal.

From a geometric analysis of mechanical models of irregular packing, Bernal concluded that the most important characteristic of the structure of a simple liquid, distinguishing it from a crystal, is related to the existence of a five-fold rotational axis of symmetry. In fact, pentagonal faces are frequently encountered in the VP of irregular random packing. To confirm this important characteristic of the structure for more reliable models, it is necessary to find for them the distribution of the faces of the VP with respect to the number of sides. Calculations carried out by the MC [10] and MD [19] methods in fact detected a predominance of pentagonal faces in the Voronoi polyhedra for a liquid. It would appear that an essential feature of the structure of a liquid had been reliably determined, but computer calculations[10] raised some doubt about this. The fact is that pentagonal faces are most frequently encountered in the VP not only for instantaneous configurations of the liquid, but also for the crystal. The factor leading to the predominance of five-fold symmetry in both disordered and regular structures has still to be determined. It is natural to relate it to the thermal motion of the atoms. Five-fold symmetry, inadequate for the crystal, can be avoided by changing from an analysis of instantaneous configurations of the particles to an examination of configurations averaged with respect to time.

This method of averaging for a crystal with a large atom settling time is quite acceptable, and gives a positive result. The elements of five-fold symmetry disappear for an averaging time $\tau \gg \tau_0$, where τ_0 is the period of the vibrational motion of the atoms. In a liquid, however, in contrast to a crystal, there are no equilibrium positions of vibrational

motion of the atoms. With developed translational motion of the atoms, averaging over a large time interval may lead to an unnatural configuration with marked overlap of the particles#. This can be avoided by decreasing the averaging time interval, but there is no guarantee that this procedure corresponds to the desired goal.

Averaging with respect to a short time interval was also carried out for the configurations of particles obtained in the MD model of a liquid[77]. The averaging time[77] was 5×10^{-13} s for a time step $\Delta t = 10^{-14}$ s. Displacement of the particles of the immediate environment in a liquid cannot take place in this short time interval. The particles are displaced on the average a distance $r \leqslant 0.1\sigma$. The time of 5×10^{-13} s is close to the average period of the vibrational motion of the atom in a liquid, so that the configurations of the particles, averaged over this time interval, should not differ greatly from the instantaneous configuration§.

Thus in the study of the structure of an equilibrium liquid, direct averaging with respect to time is not effective. To obtain structural characteristics which show little sensitivity to thermal fluctuations, another method of analysis using VP was proposed independently[55,96]. In a study of the crystallisation of supercooled argon, to record the face-centred cubic structure more accurately, small edges ($l \leqslant 0.3\sigma$) in the VP were excluded[55].

To establish the differences in the arrangement of the nearest neighbours in a simple liquid and a crystal, the small faces and edges in the VP were excluded[86]. The application of this procedure to the VP for crystalline argon brings the n- and m-distributions closer to the results obtained by averaging with respect to time. This indicates the physical justification (acceptability) of the procedure involving the rejection of the small edges and faces. The n- and m-spectra of liquid and crystalline argon, constructed after excluding the small geometric elements (see Figs.15 and 16), differ considerably. Thus the difference between the dispersions of the n- and m-distributions of the liquid and the crystal increased by average factors of 2.5 and 3.5 respectively. The proportion of pentagonal faces in the VP for the liquid remained high, whereas for the crystal it decreased considerably. After excluding the faces with $s \leq 0.2\bar{s}$ and the edges with $l \leq 0.4\bar{l}$, four-sided faces predominate in both the crystal and the liquid. The ratio of the numbers of five- and four-sided faces was 0.81 in the liquid, however, whereas for the crystal it was 0.14.

#In the case of liquid argon, the averaging time should be shorter than the time $\tau_\sigma = 1 \times 10^{-11}$ s, after which the particle is displaced on the average through a distance σ.

§The results of an analysis of VP constructed for the instantaneous configurations of the particles of the MD model of liquid Al at the melting point and with superheating by ~200 K have been interpreted[85] as confirming the possibility of structural transformations in the melt, analogous to the transformations in the solid phase. The face-centred cubic and body-centred cubic phases were detected in the melt[85] only from the topological characteristics of the VP, but the dimensional (metric) characteristics of the VP were not examined. This method of identifying the structure is not unambiguous[55]. Even if it is assumed that the proportions of VP of the face-centred cubic and body-centred cubic types have been determined correctly, it can still hardly be concluded that a structural transformation takes place in the melt, since the number of VP of these types is small (reaching ~5%).

If the system is compressed and cooled rapidly, the vitreous state of the element is produced in the MD model[52,57]. In this case the particles undergo only vibrational motion about the irregular equilibrium positions, and in the structural analysis it is possible to study the configurations of the particles averaged with respect to time. A comparison of the configurations, averaged with respect to time, of regular and irregular face-centred cubic and body-centred cubic structures has been carried out[57]. The n- and m-distributions for these configurations, shown in Fig.17, were obtained with an averaging time $\tau \cong 8 \times 10^{-11}$ s and 3×10^{-11} s for vitreous argon and the ordered structures respectively. The differences in the spectra are obvious. The dispersion of the n-distribution for the irregular structure is 6.5 times that for the face-centred cubic structure. Pentagonal faces predominate in the m-distribution of vitreous argon. Four-sided faces predominate in the face-centred cubic crystal, and hexagonal faces in the body-centred cubic crystal. The structure of vitreous argon was found to be non-uniform. Its spatial non-uniformity is reflected by the VP, shown in Fig.18. The shape and size of the Voronoi polyhedron characterising the intermediate "structural granule" (Fig.18*b*) are close to those of the most probable VP for an equilibrium liquid at the melting point; the differences between their volumes and surface areas are very small (~0.7% and 2.2% respectively). The intermediate configuration has a distorted structure, and its dimensions are smaller than those of the critical crystalline nucleus, which contains ~50 particles[53].

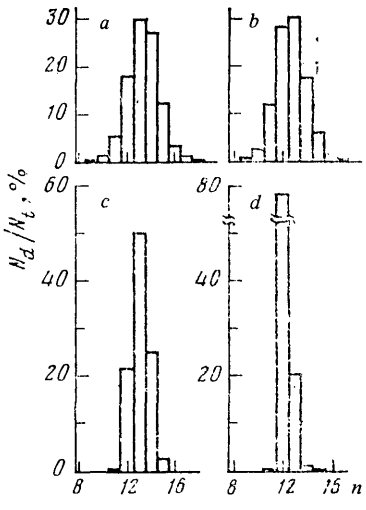


Figure 15. Distribution of VP with respect to the number of faces before (left) and after exclusion of the faces with area $s \leqslant 0.2\bar{s}$ [86] (*a*, *b*—spectra of liquid argon at 83.7 K; *c*, *d*—crystalline argon at 81.1 K); N_d/N_t is the relative number of VP with a definite number of faces.

Yet another method for determining the structural differences in the short-range order of a liquid and a crystal has been proposed[87]. This version of the structural analysis involves not the direct comparison of the packing

of particles in a liquid and a crystal, but an intermediary—an ideal crystal lattice corresponding to an average density $\rho = N/V$. The essential feature of the method is the mapping of the particles in the model on to the sites of this lattice. The number of sites is greater than the number of particles mapped on to them. The lattice penetrates the sphere distinguished in the basic MD cell. The sphere is drawn around one of the particles selected randomly in the calculation. For the liquid, this procedure is repeated after every 50 time steps ($\Delta t = 10^{-14}$ s); the total calculation time is 5×10^{-12} s. In the case of the crystal, one configuration of the particles was analysed. The volume of the sphere contained the particles of the first two coordination spheres in the liquid (an average of 57 particles), and three in the crystal (43 particles). The central particle was superimposed on a site of the lattice; for the other particles present in the sphere, the distances to the nearest sites of the lattice were determined. With this correspondence between the particles and the lattice sites, two or even three particles of the liquid were assigned to some of the sites.

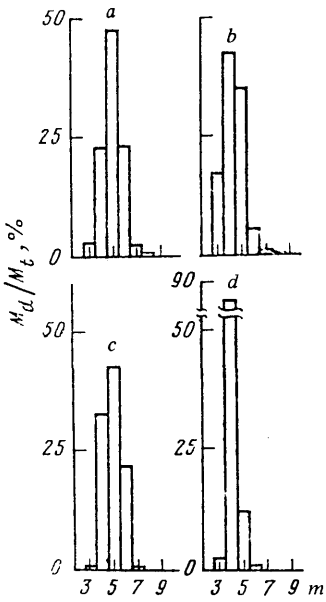


Figure 16. Distribution of the faces of the VP with respect to the number of faces without restriction on l and s (left) and with the exclusion of edges with $l \leq 0.4\bar{l}$ and rejection of faces with $s \leq 0.2\bar{s}$;[86] *a–d*) see Fig. 15; M_d/M_t is the relative number of faces with a definite number of sides.

Another method of mapping involves searching for the nearest unoccupied site for each particle. In this case a one-to-one correspondence was achieved between the particles and the lattice sites. The configurations of the particles averaged over time intervals of 5×10^{-13} s for the liquid and 10^{-11} s for the crystal were analysed. The results of the mapping of the particles on to the sites of a face-centred cubic lattice are shown in Fig. 19 (N_r/N_t denotes the relative number of particles situated at a distance Δr from the lattice sites, and d the distance between nearest neighbours in the ideal face-centred cubic lattice). For a liquid, two distributions with respect to the distances from the lattice sites are obtained, depending on the method of mapping. For a crystal there is only one distribution, independent of the method of mapping. The distribution for the liquid, corresponding to one-to-one mapping, extends as far as distances greater than d. The proportion of particles which for the transformation to a regular structure must be moved through distances greater than d is ~0.7%. This means that it is impossible to obtain the crystal from the liquid only by local displacements of the atoms. In exactly the same way it is impossible to obtain the liquid from the crystal by random small displacements of the particles from the lattice sites (blurred lattices). An appreciable proportion of the atoms in these transitions are displaced through a distance of the order of the interatomic distance.

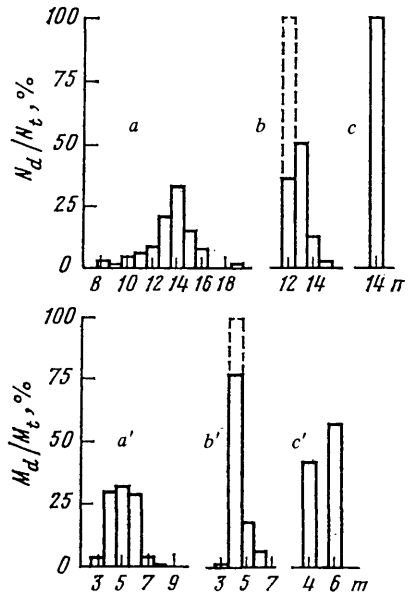


Figure 17. Distribution with respect to the number of faces of the VP and of faces with respect to the number of edges[57]: *a,a'*) vitreous argon at 48.8 K; *b,b'*) face-centred cubic crystal at 41.4 K; *c,c'*) body-centred cubic crystal at 48.4 K; Broken line—ideal face-centred cubic lattice.

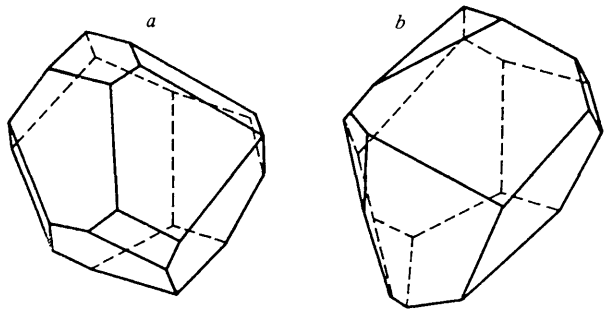


Figure 18. Voronoi polyhedra for the averaged configuration of vitreous argon[57]: *a*) for one of the particles of the uniform part of the volume; *b*) for a particle in the region of the "structural granule".

The results[57,86,87] obtained by the MD method do not confirm the quasi-crystallinity concept in the theory of the liquid state. This is also indicated by the experimentally observed avalanche-like character of the phenomenon of crystallisation and the extensive supercooling of liquids. The structure of the short-range order is different for a liquid and for a crystal. For the production of a crystal-like nucleus in a liquid, "continuous" local rearrangement of the atoms of the immediate environment of the uniform deformation type is insufficient. The conclusion from the study of random packing that five-fold symmetry plays a significant role is confirmed. When this symmetry is present, a regular crystal cannot be constructed.

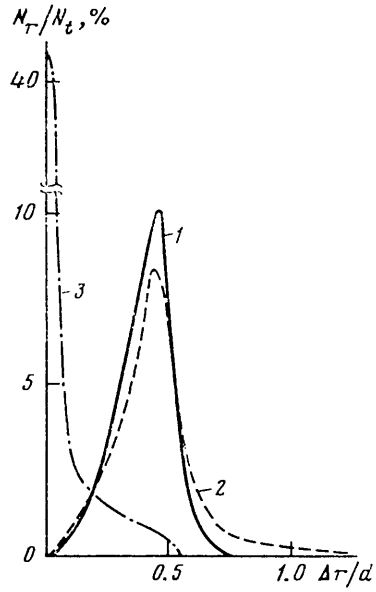


Figure 19. Radial distributions of the particles of a liquid (*1*, *2*) and a crystal (*3*) relative to the ideal face-centred cubic lattice[87]: *1*) with the possibility of repeated action of the lattice sites; *2*) for one-to-one correspondence between the particles and the lattice sites.

VI. SUMMARY

There is as yet no exhaustive answer to the question of how a liquid is constructed. The efforts of research workers are revealing new knowledge, refining old ideas, and developing an overall picture.

A liquid, as a dense irregular structure, is more unique than assumed by quasi-crystalline representations. It is characterised by more numerous and "free" local configurations than an ordered regular structure. The high mobility of the particles and the presence of small groups of particles (with a local density exceeding the crystalline density) create favourable conditions for the exchange of energy and molecular rearrangements.

Attention has been drawn[88] to the structural aspect of chemical transformations in a condensed phase. The principal restriction on the reaction rate is seen in the deficit of free volume for the reacting atoms, and their low mobility. The value of the activation energy in this sense can be regarded as "generalised" and it is not always an exact indicator of the structural-dynamic restrictions in chemical kinetics. The variety of packings of the particles in a liquid is revealed in the excess entropy of the state compared with the crystal. An adequate theory of the elementary chemical act must be constructed with allowance for the local structural-dynamic characteristics of the liquid.

New and interesting facts have been observed in the study of the kinetics of chemical transformations at low temperatures[89]. The reaction rate in the liquid phase decreases with decrease in temperature. When the solution is frozen, however, in some cases it begins to increase very strongly, reaches a maximum, and decreases again on further cooling of the system. This behaviour is not exceptional; it is observed for many reactions involving substitution, decomposition, oxidation, and polymerisation[89]. A significant role in the kinetics of a transformation is apparently played by the phase non-uniformity of multi-component systems. Because of this, conditions are created for the high mobility of groups of particles. The high mobility has been related[89] to the existence of local liquid-like regions ("liquid microphase") in the heterogeneous frozen system. The new facts necessitate a detailed analysis of the structural-dynamic causes of the "anomalous" chemical behaviour of solutions in the region of the heterogeneity and the phase transformation. The state of the supercooled liquid permits a large number of local rearrangements of the particles in a large number of configurations of the non-crystalline type. Decrease in temperature most frequently leads of the production of very compact formations of several molecules, facilitating chemical reaction.

The structure of simple liquids exhibits a certain universality. This is reflected in the existence of thermodynamic similarity in the properties of substances in the liquid state. The marked difference in various properties of metallic and non-metallic liquids is due chiefly to the influence of the electronic sub-system.

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Palladium(I) Complexes in Coordination Chemistry and Catalysis

O.N.Temkin and L.G.Bruk

The state of a rapidly developing branch of the coordination chemistry of platinum metals, namely the chemistry of palladium(I) complexes, is examined. The fundamental properties, chemical reactions, and methods of synthesis of palladium(I) complexes are described. The role of palladium(I) compounds in the mechanisms of catalytic and stoichiometric reactions is discussed.
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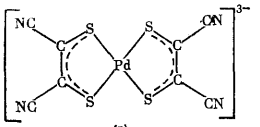
I. INTRODUCTION

Complexes of metals with the d^9 electronic configuration are known for the metals at the ends of the transition series in the Periodic System. Until recently, the family of these compounds was limited mainly to copper(II) and zerovalent cobalt complexes[1]. Although the first representatives of the coordination compounds of the nickel triad in the +1 oxidation state have been known for a fairly long time [nickel(I)—1913 [2] and palladium(I)—1942 [3]], the early studies concerning palladium(I) complexes have been treated with much scepticism. For example, there is not even a mention of palladium(I) in the monograph of Cotton and Wilkinson[1] (1965), while Livingstone's book[4] (1973) describes three complexes and notes that "the existence of univalent palladium still cannot be regarded as proved". Only Maitlis's monograph[5] (1971) presents complete information about all the few compounds of formally univalent palladium known at the time.

During the last ten years, numerous studies concerning nickel(I), palladium(I), and platinum(I) have been published, the early investigations have been re-examined, and it has become possible to speak of a new family of complexes of formally univalent nickel, palladium, and platinum. The interest in these compounds has been to a large extent stimulated by studies in the field of metal complex catalysis and in the chemistry of cluster compounds. It was found that the complexes of the metals M(I) of the nickel triad contain a wide variety of σ and π ligands and have a series of rarely encountered structural features. The present review is devoted to palladium(I) compounds whose structure and reactivity have been investigated most fully.

II. THE STRUCTURE AND PHYSICAL PROPERTIES OF PALLADIUM(I) COMPLEXES

By the beginning of 1981, more than 140 palladium(I) compounds with various σ and π ligands had been synthesised. In the vast majority of instances the palladium(I) complexes are dimeric as a result of the formation of Pd—Pd bonds and are diamagnetic in contrast to the numerous monomeric paramagnetic nickel(I) complexes[6,7]. Only one monomeric paramagnetic palladium(I) [and platinum(I)] complex (I) with a chelating thiolene ligand is known[8].



(I)

Furthermore, the formation of paramagnetic Pd^+ ions has been detected by EPR on the PdY zeolite under various conditions[9,10]. The most thoroughly investigated class of cluster complexes of palladium comprises dimers with the Pd_2^{2+} fragment, although complexes containing the following skeletons made up of palladium atoms are already known: Pd_2^{2+}, Pd_3^{2+},[11,12] Pd_3^{4+},[13-15] Pd_4^0,[16] Pd_4^{4+},[17-21] Pd_5^{4+},[22] Pd_{10}^0,[23] Pd_{10}^{8+},[24] and Pd_{12}^0.[25]

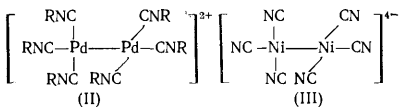
The formal oxidation state of the metal atom in the complex is defined, according to Nyholm[26], as the charge which remains on the group of metal atoms after the removal of the ligand and is referred to the number of metal atoms. It is assumed that in the leaving ligand atoms or groups of atoms (H^-, Cl^-, O^{2-}, OH^-, NH_2^-, PR_2^-, $SnCl_3^-$, CH_3^-) the electron cloud of the atom linked to the metal corresponds to the cloud of the nearest inert gas atom and that the ligands are removed in the form of neutral molecules (CO, NO, N_2, CO_2, C_2H_2, C_4H_4). Certain π-bonded organic groups (C_3H_5, C_5H_5) are believed to be anions like the σ-bonded groups ($C_3H_5^-$, $C_5H_5^-$). From this standpoint, the oxidation state of palladium in the compounds C_3H_5PdCl, $(C_3H_5)_2Pd$, and C_5H_5PdCl is +2, while in the compounds $C_3H_5Pd_2Cl$, $(C_3H_5)_2.Pd_2$, and $C_5H_5Pd_2C_3H_3$ it is +1. In view of the foregoing, compounds containing Pd^+, Pd_2^{2+}, and Pd_4^{4+} belong to the class of complexes of formally univalent palladium (+1 oxidation state). These complexes will be considered in the present review.

1. Palladium(I) Complexes with σ-Ligands

In this subsection we shall deal with palladium(I) complexes containing ligands which supply to the metal unshared σ (or *n*) electron pairs and are linked to the metal via a single centre (atom)†.

†In contrast to the π-ligands which form π-complexes, ligands of this kind can be usefully referred to as σ-ligands regardless of the predominant direction of electron transfer in the M—L bond and its multiplicity. Ligands containing π-electron pairs as well as σ-electron pairs can naturally be coordinated as π-ligands or as both σ- and π-ligands simultaneously (RCN, RNC, N_2, CO, CS_2).

Palladium(I) complexes with isonitriles (Table 1) are the most stable among the palladium(I) compounds with σ-ligands. This factor as well as the possibility of growing their single crystals made it possible in 1974 to carry out the first X-ray diffraction study on the palladium(I) complex with a σ-ligand: $[Pd_2(CH_3NC)_6](PF_6)_2 \cdot \frac{1}{2}(CH_3)_2CO$.[27,28] A characteristic feature of the structure of the complexes $Pd_2(RNC)_6^{2+}$ (II) as well as the analogous nickel(I) complex $Ni_2(CN)_6^{4-}$ (III) [29] is a square planar environment of the metal atom:



(II) (III)

This structure is apparently characteristic of all dimeric palladium(I) complexes with σ-ligands.

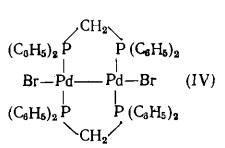
Table 1. Palladium(I) complexes with isonitrile ligands.

Complex	X	L	L′	Refs.
$[PdXL_2]_2$	Cl, Br, I	t-C_4H_9NC	—	[30, 31]
$[PdXL_2]_2$	I	CH_3NC, C_6H_5NC	—	[31]
$[PdXL_2]_2$	SCN	CH_3NC	—	[31]
$[PdXL_2]_n$	Cl, Br	CH_3NC	—	[32]
$[PdXL]_2$	I	t-C_4H_9NC	$P(C_6H_5)_3$	[30]
$[Pd_2L_6]X_2$	PF_6, Cl	CH_3NC	—	[27, 28]
$[Pd_2L_6]X_2$	Br	t-C_4H_9NC	—	[32, 33]
$[Pd_2L_6]X_2$	Br	C_6H_5NC	—	[32, 33]
$[Pd_2L_5L'](PF_6)_2$	—	CH_3NC	$P(C_6H_5)_3$	[33]
$[Pd_2L_4L_2'](PF_6)_2$	—	CH_3NC	$P(C_6H_5)_3$	[33]
$[PdPtL_6](PF_6)_2$	—	CH_3NC	—	[33, 34]
$[PdPtL_5L'](PF_6)_2$	—	CH_3NC	$P(C_6H_5)_3$	[31, 33]
$[PdPtL_4L_2'](PF_6)_2$	—	CH_3NC	$P(C_6H_5)_2$	[31, 33]
$[Pd_2L_2L_2'](PF_6)_2$	—	CH_3NC	$(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$; $n=2-4$	*
$[Pd_2L_2L_2'](PF_6)_2$	—	CH_3NC	$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$	*

*C.H.Lindsay, L.S.Benner, and A.L.Balch, Inorg.Chem., 1980, 19, 3503.

A typical feature of the complexes of isonitriles is the absence of bridge ligands, which, together with the diamagnetism and the short Pd–Pd distance (2.53 Å) makes it possible to infer with confidence the presence of a metal–metal bond. Thus the complexes are dsp^2 hybridised and the fourth coordination site at each palladium atom is occupied by a neighbouring palladium atom. The angle between the planes in which the PdL_3 groups are located is 86.2° for L = CH_3NC.[27,28]

Certain bidentate σ-ligands#, namely CH_3COO^-, $CH_2[As(C_6H_5)_2]_2$, and $CH_2[P(C_6H_5)_2]_2$, are bridge ligands in complexes with Pd–Pd bond (Table 2). In the case of bridge phosphine the angle between the planes of the PdL_3 groups is 39° (38.5° in the platinum analogue). However, the virtually square planar coordination around each palladium atom is retained[49]. The Pd–Pd distance in the complex $Pd_2Br_2dpm_2$ (IV) is 2.699 Å.[49]



(IV)

#Henceforth $CH_2[As(C_6H_5)_2]_2$ and $CH_2[P(C_6H_5)_2]_2$ will be designated by *dam* and *dpm* respectively.

We shall consider in greater detail the carbonyl complexes of palladium(I).[52] During the time since the publication of the first study[53], a large set of carbonyl halide complexes of palladium have been obtained under similar conditions from CO and PdX_2 with an average degree of oxidation from +0.5 to +2, which was calculated from the determinations of the contents of the elements[35–41,53–57]. According to the majority of investigators, these compounds are coordination monomers of the type $Pd_m(CO)_lX_n$. The insoluble polymeric complexes have been synthesised by various investigators and had similar spectroscopic characteristics but differed significantly in composition. It has been established[38,39] that the composition and properties of the coordination polymers are determined to a large extent by the amount of water in the reaction medium during their synthesis. The influence of the water concentration on the composition of the complexes and hence on the average degree of oxidation of palladium is apparently related to the involvement of water in the stages involving the reduction of palladium(II) and palladium(I) to zerovalent palladium via reaction (1). The interaction of the carbonyl complexes of palladium(I) with PdX_2 and Pd(0), whose ratio in the reaction system depends on the concentration of water, proceeds via Scheme (2) and leads to coordination polymers with different degrees of oxidation of palladium:

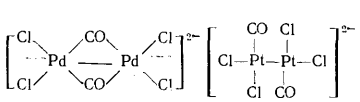
$$PdX_2 \xrightarrow{CO,H_2O} Pd^0 \xrightarrow{PdX_2} Pd_2X_2(CO)_n \xrightarrow{CO,H_2O} 2Pd^0 \quad (1)$$

$$m\,Pd_2X_2(CO)_n \begin{cases} \xrightarrow{n PdX_2} Pd_{(2m+n)}X_{2(m+n)}(CO)_n \\ \xrightarrow{p Pd^0} Pd_{(2m+p)}X_{2m}(CO)_n \end{cases} \quad (2)$$

When certain conditions are maintained, it is possible to obtain polymeric complexes having the composition $(PdCOX)_n$ (Table 2, Nos.1–9).

Together with these compounds, numerous dimeric diamagnetic compounds have been synthesised, the first representatives having been obtained as early as 1942 [3] (Table 2, Nos.31–33).

A detailed study of the structures of palladium carbonyl halides by infrared and Raman spectroscopy threw some light on the question, which had been under discussion for a long time, whether the halide or the carbon monoxide functions as the bridge in the palladium(I) carbonyl halide complexes[41]. According to Goggin and Mink[41], the carbonyl groups constitute the bridges in the dimeric palladium carbonyl halides $[Pd_2(CO)_2X_4]^{2-}$ [structure (V)], while the polymeric complexes consist of dimers linked by halide bridges. It is of interest to note that the dimeric platinum(I) carbonyl halide complexes have the non-bridge structure (VI),[58,59] characteristic of palladium(I) isocyanides, in contrast to the analogous palladium(I) complexes.



(V) (VI)

The first palladium(I) carbonyl acetate cluster of the type $[Pd(CO)(OOCCH_3)]_4 \cdot 2CH_3COOH$ was obtained in a number of studies[17–19] (Table 2, Nos.10 and 14). The crystal of this compound is made up of planar tetranuclear complexes (VII) and acetic acid dimers located at the centres of symmetry. The complex (VII) contains two dimeric complex species $Pd_2(CO)_2^{2+}$ with Pd–Pd bonds (l = 2.663 Å) and carbonyl bridges linked via four acetate groups[42]. Moiseev et al.[19] and Kuz'mina and Struchkov[42] carried out the first X-ray diffraction studies on palladium(I) carbonyl complexes.

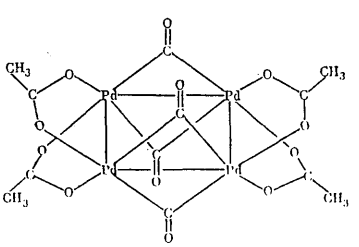
Table 2. Palladium(I) complexes with CO and other σ-ligands.

No.	Complex	X,	L′,	M+	$\nu_{CO,\,NO}$ cm^{-1}	References
			$[Pd(CO)X]_n$			
1	Pale yellow	Cl	—	—	2003, 1972, 1942	[35]
2	Yellow-green or red-violet	Cl	—	—	1975, 1925, 1892	[36]
3	Yellow-green	Cl	—	—	1978, 1940	[37]
4	Yellow, violet	Cl	—	—	1985, 1975, 1960, 1940	[38]
5	Yellow-brown	Cl	—	—	1977	40]
6	Yellow-green	Cl	—	—	2023, 2002, 1978, 1951, 1936	[41]
7	—	Br	—	—	1960, 1930	[38, 39]
8	Bright green	Br	—	—	1953	[40]
9	Yellow	Br	—	—	2008, 1996, 1987, 1953, 1938, 1922	[41]
10	$n = 4$	CH_3COO	—	—	1975, 1940	[17—19]
11	$n = 4$	C_2H_5COO	—	—	1968, 1935	[19]
			$[Pd(CO)X]_nL_m$			
12	Yellow; $n = 6, m = 2$	Cl	C_6H_5CN	—	1979, 1954c, 1948c, 1917	[41]
13	Brown; $n = 2, m = 2$	Cl	$As(C_6H_5)_3$	—	1963, 1918, 1890, 1961, 1816	[41]
14	Yellow; $n = 4, m = 2$	CH_3COO	CH_3COOH	—	1975, 1934	[17—19, 42]
15	$n = 4, m = 2$	CD_3COO	CD_3COOD	—	1965, 1931	[17—19]
16	$n = 4, m = 2$	C_6H_5COO	C_6H_5COOH	—	1980, 1958	[17—19]
			$Pd_4(CO)_2L_nX_4$			
17	Black; $n = 4$	CH_3COO	phen	—	1800	[20, 21, 43]
	»	Cl, CCl_3COO	phen	—	—	[44]
	»	CF_3COO, CNS	phen	—	—	[44]
18	Brown; $n = 2$	CH_3COO	bipy	—	1800	[44]
19	Brown		$[(PdXL)_2CO]_n$			
20	Brown	Cl	$P(C_6H_5)_3$	—	1892, 1962	[45, 46]
20a	Dark cherry-red	Br	$P(C_6H_5)_3$	—	1890, 1860	[45, 46]
21	Brown	I	$P(C_6H_5)_3$	—	1902, 1862	[45, 46]
22	Red	Cl	$P(C_6H_5)(p\text{-}CH_3OC_6H_4)_2$	—	1889, 1859	[45, 46]
		Br	$P(C_6H_5)(p\text{-}ClH_3OC_6H_4)_2$	—	1891, 1864	[45, 46]
23	Dark red	Cl	$P(C_6H_5)_2(C_6H_4COOH)$	—	1898, 1867	[45, 46]
24	Bright red	Br	$P(C_6H_5)_2(C_6H_4COOH)$	—	1893, 1865	[45, 46]
25	Pale brown	Cl	$P(C_6H_5)_2(C_6H_4F)$	—	1893, 1859	[45, 46]
26	Red brown	Br	$P(C_6H_5)_2(C_6H_4F)$	—	1896, 1861	[45, 46]
27	Brown	Cl	$P(C_6H_5)_2(C_6H_4Cl)$	—	1892, 1860	[45, 46]
28	Red brown	Br	$P(C_6H_5)_2(C_6H_4Cl)$	—	1890, 1861	[45, 46]
29	Brown	Cl	$P(C_6H_5)_2(C_6H_4CH_3)$	—	1890, 1860	[45, 46]
30	Red brown	Br	$P(C_6H_5)_2(C_6H_4CH_3)$	—	1898, 1870	[45, 46]
			$[Pd_2(CO)_2X_4]M_2$			
31	Greenish yellow	Cl	—	NH_4	—	[3]
32	Bright yellow	Cl	—	$Pt(NH_3)_4^{2+}$	—	[3]
33	Yellow	Cl		$(CH_2NH_3)_2^{2+}$	—	[3]
34	Pale yellow	Cl	—	Cs	1915	[40]
35	Green	Cl	—	Rb	—	[40]
36	Greenish yellow	Cl	—	$(n\text{-}C_3H_7)_4N$	1962, 1973, 1905—1922	[41]
37	Yellow	Cl	—	$(n\text{-}C_4H_9)_4N$	1960—1966, 1898—1907	[41]
38	Brown	Br	—	Cs	1947, 1893, 1869	[40]
39	Orange	Br	—	$(n\text{-}C_3H_7)_4N$	1958—1966, 1903—1905	[41]
40	Yellow-orange	Br	—	$(n\text{-}C_4H_9)_4N$	—	[41]
41	$[Pd_4Cl_6(CO)_4][(n\text{-}C_3H_7)_4N]_2$	—	—	—	1964, 1918, 1906	[41]
			$[Pd(NO)Cl]_n$			
42	Dark brown	—	—	—	1764, 1712	[47]
43	Pale brown	—	—	—	1750, 1720	[48]
44	Pale green; $[Pd(NO)Cl]PdCl_2$	—	—	—	1672	[48]
45	Black; $(PdCl)_2NO$	—	—	—	1665	[48]
			$Pd_2(L—L)_2X_2$			
46	—	Cl, Br	dam	—	—	[40]
47	—	Cl, Br	dpm	—	—	[49]
48	—	I	dpe	—	—	[30]
48a	—	PF_6	tpde	—	—	*
			$Pd_2L_nX_2$			
49	Brown; $n = 1$	CH_3COO	bipy	—	—	[44]
50	$n = 2$	CH_3COO	$P(C_6H_5)_3$	—	—	[50]
51	Yellow-green; $n = 2$	SCN	$P(C_6H_5)_3$	—	—	[45]
			$Pd_2I_4M_2 \cdot 2H_2O$			
52	Black	—	—	Li	—	[51]
53	Black	—	—	Cs	—	[51]

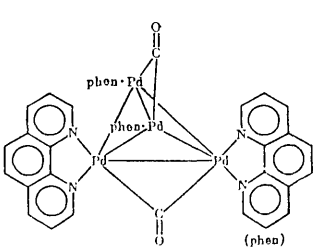
Notation: phen = *o*-phenanthroline; bipy = α,α′-bipyridyl; dpe = bis(diphenylphosphino)-ethane; tpde = $(C_6H_5)_2P(CH_2)_2P(C_6H_5)(CH_2)_2P(C_6H_5)_2$.

*C.H.Lindsay, L.S.Benner, and A.L.Balch, Inorg.Chem., 1980, **19**, 3503.

The same workers obtained a tetranuclear cluster (Table 2, No.17) with a tetrahedral Pd_4^{4+} skeleton[20,21]. X-Ray diffraction analysis of the complex $Pd_4(CO)_2(phen)_4(OOCCH_3)_4$ (VIII) showed that all four palladium atoms are equivalent and form an almost regular tetrahedron. The two Pd–Pd bonds having carbonyl bridges (the Pd–C–Pd angle is 105°) are somewhat longer (l_{Pd-Pd} = 2.890 Å) than the four Pd–Pd bonds without such bridges (2.718 Å). *o*-Phenanthroline behaves as a bidentate terminal ligand; the acetate ions are in the inner sphere of the complex[20,21].



(VII)



(VIII)

Solutions of palladium(I) carbonyl halide complexes in concentrated hydrochloric acid, obtained by the method of Colton et al.[40] and Goggin and Mink[41], were used[45,46] to synthesise the complexes $[(PdLX)_2CO]$ (Table 2, Nos.19–30). After being dried in an atmosphere of argon, these complexes are entirely stable but in solution in benzene, acetone, and ethanol they slowly disproportionate (the formation of colloidal, metallic palladium is observed). They contain only one carbonyl group for two palladium atoms and have a large dipole moment (μ = 7–9 D) and reduced stretching vibration frequencies ν(CO) of the carbonyl group (Table 2). Furthermore, their ^{31}P NMR spectra contain two bands with the chemical shifts δ_1 = −22 – −24 p.p.m. and δ_2 = −19 to −21 p.p.m., which apparently indicates different types of coordination of the two phosphine ligands[46].

In conclusion we shall consider briefly the possibility of using the parameters of the infrared spectra, in particular the frequencies ν(CO), for the analysis of the structure of the complex and the determination of the oxidation state of the metal. The range of variation of ν(CO) for the palladium and platinum complexes is very large, reaching ~500 cm^{-1}.[60,61] The main factors influencing ν(CO) are (a) the nature of the coordination of the CO group (terminal or bridge groups), (b) the type of bridge, (c) the degree of oxidation of the metal (metals), and (d) the nature of the other ligands. The influence of the degree of oxidation of platinum and palladium on ν(CO) can be traced from the following examples. The change in the stretching vibration frequency of the terminal CO group $\Delta\nu$(CO) on passing from platinum(II) to platinum(0) is ~30 cm^{-1} and that on passing from platinum(II) to platinum(I) is 52–71 cm^{-1} (Table 3). Similarly in the case of the Pd(II) → Pd(0) transition the value of $\Delta\nu$(CO) is low (~70 cm^{-1}). The change in the type of coordination (transition from the terminal to the bridge CO group) leads to a considerable decrease of ν(CO).

Table 3. The influence of the degree of oxidation of the metal and of the type of coordination of carbon monoxide on ν(CO).

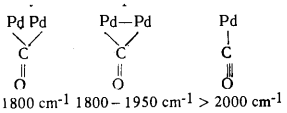
Metal (degree of oxidation)	Complex	ν(CO), cm^{-1}	References
Pt(II)	$PtCl_3(CO)^-$	2098	[61]
Pt(I)	$Pt_2(CO)_2Cl_4^{2-}$	2047, 2027	[58]
Pt(0)	$[Pt(CO)_2]_n$	2068	[58]
Pd(II)	$PdCl_3(CO)^-$	2132	[61]
Pd(I)	$Pd_2(CO)_2Cl_4^{2-}$	1922, 1973	[41]
Pd(0)	$Pd(CO)_4$	2060	[62]

Thus ν(CO) for the dimer $[Pd_2(CO)_2Cl_4]^{2-}$ is reduced compared with ν(CO) for $[PdCl_3CO]^-$ by 210–160 cm^{-1}, while the decrease of ν(CO) as a consequence of the change in the oxidation state of palladium [Pd(II) → Pd(I)] should not exceed 70 cm^{-1}. The vibration frequencies of the CO group coordinated as a bridge at the Pd–Pd bond in palladium(I) complexes are in the range 1800–1980 cm^{-1}.[16–21,23,41] This wide range of ν(CO) is apparently associated with the number of CO groups (strong π-acceptors), coordinated to the Pd_2 group, and with the characteristics of the Pd_2CO fragment (the Pd–C–Pd angle and the Pd–Pd bond length) rather than with the influence of other ligands. Thus ν(CO) for the complexes $[Pd(CO)(OOCCH_3)]_4$, $[Pd(CO)Cl]_n$, and $[Pd_2(CO)_2Cl_4]^{2-}$ are in the range 1900 to 1980 cm^{-1}, while those for the complexes $(PdLX)_2CO$ or $[Pd_4(CO)_2Phen_4]^{4+}$ are in the range 1800–1890 cm^{-1}. The vibration frequencies of the CO groups coordinated in the form of bridges in the zerovalent palladium clusters are in the same range[16,23]. There is no doubt that there is a correlation between ν(CO) and the characteristics of the Pd_2CO fragment—the Pd–C–Pd angle of the Pd–Pd bond length (Table 4). In the limiting case (Table 4, No.5) CO is inserted in the Pd–Pd bond, the Pd–C–Pd angle is ~120°, and ν(CO) has the usual values characteristic of the carbonyl group in organic compounds (see Section III, subsection 4).

Table 4. Relation between ν(CO) and the characteristics of the Pd_2CO fragment.

No.	Complex	ν(CO), cm^{-1}	l_{Pd-Pd}, Å	$\alpha_{Pd-C-Pd}$, °	l_{Pd-C}, Å	Refs.
1	$[Pd(CO)CH_3COO]_4$	1940, 1975	2.663	84.5	1.99	[18,19,42]
2	$Pd_4[P(C_6H_5)_2CH_3]_4(CO)_4$	1840, 1820	2.75	82.5	2.085	[16]
3	$Pd_{10}(CO)_{12}[P(n\text{-}C_4H_9)_3]_6$	1800, 1853, 1890	2.70; 2.82	83	2.05	[23]
4	$[Pd_4(CO)_2phen_4]^{4+}$	1800	2.890	105	—	[20, 21]
5	$[Pd(dam)Cl]_2CO\cdot 3C_6H_{14}$	1720	3.274	119	1.9	[63]

Thus the following limiting frequencies ν(CO) can be used for a preliminary assessment of the nature of the coordination of the CO group in palladium compounds on the basis of infrared spectroscopic data:



Palladium(I) complexes with terminal CO groups and palladium(II) complexes with CO groups coordinated in the form of bridges are hitherto unknown, but the frequencies ν(CO) for such compounds should apparently be within the limits indicated.

The first binary palladium(I) complex of the type $M_2Pd_2I_4 \cdot 2H_2O$, where M = Li or Cs, has been synthesised[51] from the complex $H_2Pd_2(CO)_2Cl_4$ obtained by the method of Colton et al.[40] and Goggin and Mink[41]. These compounds are diamagnetic and are apparently coordination polymers, because they dissolve in alcohols, acetone, dimethylformamide (DMF), and tetrahydrofuran only in the presence of an excess of I^- ions. When the complex $Li_2Pd_2I_4 \cdot 2H_2O$ is treated repeatedly with deaerated concentrated hydrochloric acid in an inert atmosphere, a compound is obtained whose elemental analysis leads to the formula $(PdI \cdot H_2O)_n$.

The complex $(LPdOOCCH_3)_2$ has been obtained[52] in the study of the mechanism of the formation of the active forms of hydrogenation catalysts in the $L_2Pd(OOCCH_3)_2$–H_2 system. The complex $\boxed{Si}$–P_2–$Pd_2(OOCCH_3)_2$ with a similar composition has been synthesised by the reduction of palladium acetate immobilised on a phosphinated silica gel surface[64].

The first palladium(I) nitrosyl complex was synthesised in 1960.[47] Several other nitrosyl complexes, tentatively of palladium(I) (Table 2, Nos.43–45), were described later but their structure was not established[48,65]. It has been suggested that they are coordination polymers with Pd–Pd bonds like the complexes $[Pd(CO)Cl]_n$.

A comparatively high thermal stability of palladium(I) complexes has been noted in a number of studies (Table 5). Some of the data on the thermal stability of palladium(I) compounds (Table 5, Nos.1–9a) have been obtained as a result of visual observations and are approximate. The stability of the complexes $[Pd(CO)Cl]_n$ (Table 5, No.9b),

$Li_2Pd_2I_4.2H_2O$, and $(PdLX)_2CO$ has been investigated by the thermographic method. The degradation of the complex $Li_2Pd_2I_4.2H_2O$ is preceded by the elimination of water (120–320 °C), which is followed by the liberation of I_2 (one mole per mole of the initial compound in the temperature range 320–600 °C).[51] The first stage in the thermal transformations of the complexes $(PdLX)_2CO$ is isomerisation, carbon monoxide being split off on raising the temperature. At 300–400 °C the final decomposition of these compounds takes place[46,66]. The above data indicate the possibility of the existence of palladium(I) compounds under fairly severe conditions.

Table 5. Thermal stability of palladium(I) complexes.

No.	Complex	T_{decomp}, °C	References
1	$[PdCl(t\text{-}C_4H_9NC)_2]_2\cdot C_6H_5Cl$	150	[30]
2	$[PdCl(t\text{-}C_4H_9NC)_2]_2\cdot C_6H_6$	155	[30]
3	$[PdIdpe]_2$	300	[30]
4	$[Pd_2(t\text{-}C_4H_9NC)_6]_2(PF_6)_2$	140	[32]
5	$[(n\text{-}C_3H_7)_4N]_2[Pd_2Cl_4(CO)_2]$	155	[41]
6	$[(n\text{-}C_3H_7)_4N]_2[Pd_2Br_4(CO)_2]$	145	[41]
7	$[PdCl(CO)As(C_6H_5)_3]_2$	110	[41]
8a	$[Pd(CO)Br]_n$	120	[40]
8б	$[Pd(CO)Br]_n$	145	[41]
9a	$[Pd(CO)Cl]_n$	60	[40]
9б	$[Pd(CO)Cl]_n$	180	[37]
10	$Li_2Pd_2I_4\cdot 2H_2O$	320	[51]
11	$[PdP(C_6H_5)_3Cl]_2CO$	76; 110	[46, 66]
12	$[PdP(C_6H_5)_3Br]_2CO$	130; 130	[46, 66]
13	$[PdP(C_6H_5)_3P]_2CO$	136; 140	[46, 66]
14	$[PdP(C_6H_5)(C_6H_4OCH_3)_2Cl]_2CO$	79; 130	[46, 66]
15	$[PdP(C_6H_5)_2(C_6H_4COOH)Cl]_2CO$	40; 160	[46, 66]
16	$[PdP(C_6H_5)_2(C_6H_4F)Cl]_2CO$	60; 110	[46, 66]
17	$[PdP(C_6H_5)_2(C_6H_4Cl]_2CO$	78; 135	[46, 66]

Note. For compounds Nos.11–17, the isomerisation temperature is indicated first and the second figure denotes the temperature at which the elimination of CO groups begins.

2. Palladium(I) Complexes with π-Ligands

The π-complex of palladium(I) was synthesised in 1965 [67] by Fischer's method ($PdCl_2 + AlCl_3 + Al + C_6H_6$) (Table 6, No.1). X-Ray diffraction studies[67,68] established that complexes Nos.1 and 2 contain a Pd–Pd fragment [see structures (IX) and (X)].

Both compounds consist of centrosymmetric molecules containing benzene rings with virtually identical C–C bond lengths. Complexes Nos.1 and 2 differ in the position of the benzene rings relative to the Pd–Pd bond. In complex No.1 the two benzene rings located in parallel planes have at least two different orientations relative to the Pd–Pd bond [structure (IX)], differing from the orientation in the rings in complex No.2 [structure (X)] (Fig.1). The centres of the rings are displaced from the projection of the centre of symmetry of the complexes by 0.18 Å in structure (IX) and by 0.43 Å in structure (X).

Table 6. π-Complexes of palladium(I).

No.	Complex	Characteristic	Refs.
1	$Pd_2(C_6H_6)_2(Al_2Cl_7)_2$	$l_{Pd-Pd}=2.57$ Å dark brown	[67]
2	$Pd_2(C_6H_6)_2(AlCl_4)_2$	$l_{Pd-Pd}=2.57$ Å dark brown	[68]
3	$Pd_2(C_6H_5CH_3)_2(AlCl_4)_2$	—	[69]
4	$Pd_2[C_6H_4(CH_3)_2]_2(AlCl_4)_2$	—	[69]
5	$Pd_2(C_6H_6)_2(ClO_4)_2(H_2O)_2$	red-violet	[70]
6	$Pd_2(C_6H_6)_2(HSO_4)_2$	—	[71, 72]
7	$Pd_2(C_6H_6)(OOCCH_3)\cdot{}^1/_2Sol$ *	red	[73]
8	$Pd_2SO_4\cdot Q$ **$\cdot 3H_2O$	—	[74]

*Sol = CH_3COOH or CH_2Cl_2.
**Q = *p*-benzoquinone.

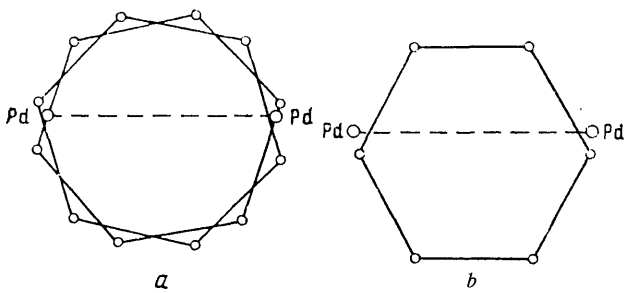
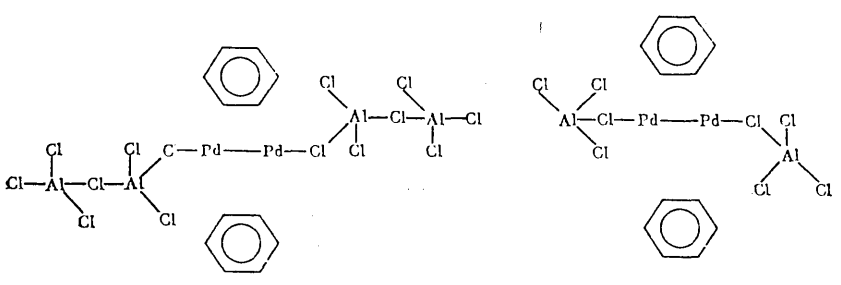
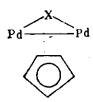
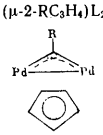
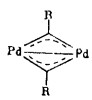
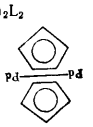
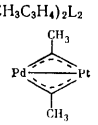
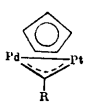
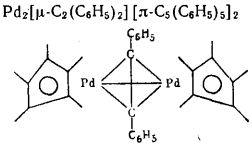


Figure 1. The disposition of the carbon atoms of the benzene rings relative to the Pd–Pd fragment in bis-π-arene complexes: *a*) complex (IX); *b*) complex (X).



The π-complexes of palladium(I) with benzene apparently have structures similar to those of complexes Nos.1 and 2 described by Davidson and Triggs[70] (Table 6, No.5) and Rudakov and co-workers[71,72] (Table 6, No.6). The studies of Rudakov and co-workers[71,72] showed that complex No.5 is diamagnetic, despite the view of Davidson and Triggs[70], and has a singlet due to benzene protons in the ^{1}H NMR spectrum, displaced upfield by 0.76 p.p.m. relative to benzene. The π-complex No.6 (Table 6) has been obtained[71,72] by the oxidation of cyclohexane or cyclohexene with palladium

Table 7. Palladium(I) complexes with allyl and cyclopentadienyl ligands.

No.	Formula	L	R	X	References
1	$Pd_2(\mu\text{-}2\text{-}RC_3H_4)(\mu\text{-}X)L_2$ 	$P(C_6H_5)_3$	H	I	[79] *
		$P(C_6H_5)_3$	H	Br	[80]
		$P(iso\text{-}C_3H_7)_3$	CH_3	I, Cl	[81, 82]
		$P(t\text{-}C_4H_9)_3$	CH_3	Cl	[81, 82]
		$P(C_6H_{11})_3$	CH_3	Cl	[82]
		$P(iso\text{-}C_3H_7)_3$	H, CH_3, *iso*-C_3H_7, t-C_4H_9	CH_3COO	[83]
		$P(iso\text{-}C_3H_7)_3$	*iso*-C_3H_7, t-C_4H_9	C_6H_5COO	[83]
		$P(iso\text{-}C_3H_7)_3$	*t*-C_4H_9	CF_3COO	[83]
2	$Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}X)L_2$ 	$P(iso\text{-}C_3H_7)_3$	—	Br	[84] **
		$P(iso\text{-}C_3H_7)_3$	—	Cl, I, $S(C_6H_5)$	[80, 84]
		$P(C_6H_5)_3$, $P(C_6H_{11})_3$	—	Br	[80, 84]
		$P(C_6H_5)_3$	—	$S(C_6H_5)$	[80]
		$P(iso\text{-}C_3H_7)_3$	—	C_6H_5COO	[85]
		$P(iso\text{-}C_3H_7)_3$	—	CH_3COO	[83]
3	$Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}2\text{-}RC_3H_4)L_2$ 	$P(C_6H_5)_3$	CH_3	—	[78] ***
		$P(OC_6H_5)_3$, $P(OCH_3)_3$	CH_3	—	[78]
		$P(C_6H_5)_3$	H, t-C_4H_9	—	[86]
		$P(C_6H_5)_2CH_3$, $P(iso\text{-}C_3H_7)_3$	CH_3	—	[86]
		$P(iso\text{-}C_3H_7)_3$, $P(C_6H_5)_2CH_3$	t-C_4H_9	—	[86]
		$P(O\text{-}o\text{-}C_6H_4CH_3)_3$	CH_3	—	[86]
		$P(O\text{-}o\text{-}C_6H_4CH_3)_3$	t-C_4H_9	—	[86] ****
		$P(iso\text{-}C_3H_7)_3$	H, Cl	—	[81]
		$P(C_6H_{11})_3$	CH_3	—	[81]
		$P(C_6H_5)(CH_3)_2$	CH_3, t-C_4H_9	—	[87]
		$P(n\text{-}C_4H_9)_3$	CH_3, t-C_4H_9	—	[87]
		$P(OCH_3)_3$, $P(OC_6H_5)_3$	t-C_4H_9	—	[87]
		$As(iso\text{-}C_3H_7)_3$, $As(CH_2C_6H_5)_3$	H, CH_3	—	[88]
		$P(CH_3)_3$, $P(iso\text{-}C_4H_9)_3$	CH_3	—	[88]
		$P(t\text{-}C_4H_9)(C_6H_5)_2$, $P(C_6H_{11})_2C_6H_5$	CH_3	—	[88]
		$P(O\text{-}iso\text{-}C_3H_7)_3$	CH_3	—	[88]
		$P(iso\text{-}C_4H_9)_3$, $P(t\text{-}C_4H_9)(C_6H_5)_2$	t-C_4H_9	—	[88]
		$P(C_6H_{11})_2(C_6H_5)$, $As(iso\text{-}C_3H_7)_3$	t-C_4H_9	—	[88]
4	$Pd_2(\mu\text{-}2\text{-}RC_3H_4)_2L_2$ 	$P(iso\text{-}C_3H_7)_3$	H	—	[80]
		$P(iso\text{-}C_3H_7)_3$	CH_3	—	[81]
		$P(C_6H_{11})_3$	CH_3	—	[82]
5	$Pd_2(\mu\text{-}C_5H_5)_2L_2$ 	$P(iso\text{-}C_3H_7)_3$	—	—	[85]
		$P(OC_6H_5)_3$	—	—	[89]
6	$PdPt(\mu\text{-}2\text{-}CH_3C_3H_4)_2L_2$ 	$P(iso\text{-}C_3H_7)_3$	—	—	[90]
7	$PdPt(\mu\text{-}2\text{-}RC_3H_4)(\mu\text{-}C_5H_5)L_2$ 	$P(iso\text{-}C_3H_7)_3$, $P(C_6H_{11})_3$	H, CH_3	—	[90]
8	$Pd_2[\mu\text{-}C_2(C_6H_5)_2][\pi\text{-}C_5(C_6H_5)_5]_2$ 	—	—	—	[77]

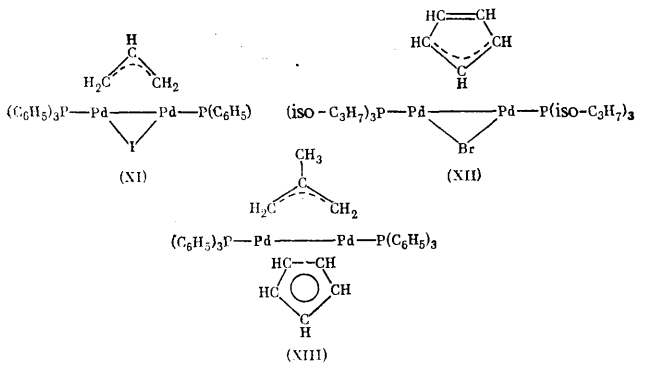
*l_{Pd-Pd} = 2.686 Å, **l_{Pd-Pd} = 2.609 Å, ***l_{Pd-Pd} = 2.679 Å, ****l_{Pd-Pd} = 2.689 Å.

sulphate and also from benzene and H_2 in 90% of sulphuric acid. Complexes Nos.5 and 6 disproportionate following the addition of Cl^- or dilution of the solutions with water.

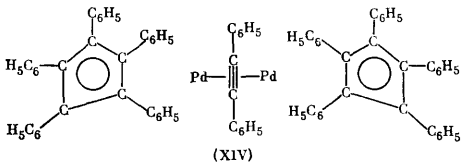
The reaction of $Pd(OOCCF_3)_2$ in CF_3COOH with benzene or naphthalene results in the formation of complexes with an involved composition[75] which the authors regard as π-arene complexes on the basis of infrared spectroscopic and NMR data as well as chemical reactions. It has been suggested that $Pd_2(OOCCF_3)_2$, formed on reduction of palladium(II), coordinates aryl groups to form $ArPdOOCF_3$.

Two π-complexes, tentatively of palladium(I) (Table 6, Nos.7 and 8), have been obtained under the conditions of the oxidation of cyclohexa-1,4-diene in acetic acid[73] and of ethylene in sulphuric acid[74] in the presence of palladium(II) salts. According to Postnikov[76], the compounds of palladium and graphite (Pd_2Cl_2-graphite) which he synthesised are π-complexes of the type of compounds Nos.1–6 in Table 6.

The palladium(I) compounds containing π-allyl and π-cyclopentadienyl ligands are also believed[32,77,78] to constitute a large group of very interesting π-complexes (Table 7). The first examples of compounds containing π-allyl and π-cyclopentadienyl ligands coordinated at an M–M bond [compounds (XI), (XII), and (XIII)] and the first examples of symmetrical bis-π-allyl and bis-π-cyclopentadienyl sandwich compounds with an M–M fragment are encountered within this group. The bond lengths l_{Pd-Pd} in these complexes are similar, exceeding slightly l_{Pd-Pd} in the bis-π-arene complex of palladium(I).



The C_5H_5 group can be regarded as one non-coordinated double bond (l = 1.331 Å) and an allyl fragment (1.48 and 1.52 Å) linked mainly to two palladium atoms (Table 7, No.2).[84] Mixed complexes with a Pd–Pt bond have been obtained as a result of the interaction of $(C_5H_5)Pt(2\text{-}CH_3C_3H_4)$ and $Pt(2\text{-}CH_3C_3H_4)_2$ with PdL_2 (Table 7, Nos.6 and 7). The interesting π-complex of palladium(I) with $(C_6H_5)_2C_2$ (XIV)



is a structural analogue of the complex $[\mu\text{-}(C_6H_5)_2C_2].Ni_2(\pi\text{-}C_5H_5)_2$.[91]

3. X-Ray Photoelectron Spectra of Palladium(I) Complexes

Relatively extensive data have now accumulated on the X-ray photoelectron (XPE) spectra of palladium(I) complexes, which permit the estimation of the range of variation of the binding energies of the palladium(I) electrons and the influence of the ligand on $E(3d_{5/2})$.[92–100] Table 8 and Fig.2 show that the ranges of variation of $E(3d_{5/2})$ for complexes containing palladium in different oxidation states (0, +1, or +2) have no distinct limits and partially overlap.

Table 8. The binding energies $E(3d_{5/2})$.

No.	Complex	$E(3d_{5/2})$, eV	References
	Pd(0)		
1	Pd_{met}	335.8	[95]
	Pd_{met}	335.7±3	[98]
2*	PdL_4	336.2	[95, 95]
3*	$Pd(CO)L_3$	337.9	[94]
4*	Pd_2L_2	336.8	[95]
	Pd(I)		
5	$Pd_2dpm_2Cl_2$	337.3	[96]
6	$Pd_2dam_2Cl_2$	337.4	[96]
7	$Pd_2dpm_2Cl_2(\mu\text{-}CO)$	337.5	[96]
8*	$Pd_2L_2(OOCCH_3)_2$	337.1	[95]
9	Pd_2Cl_2· (graphite)	336.8	[76]
10	$[PdI\cdot H_2O]_n$	336.9	**
11	$Cs_2Pd_2I_4\cdot 2H_2O$	337.3	**
12	$[Pd_2(CH_3NC)_6](PF_6)_2$	338.0	[96]
	Pd(II)		
13	$PdCl_2$	337.9±0.3	[98]
	$PdCl_2$	338.0	[76]
	$PdCl_2$	338.1	[94]
14	$PdCl_2$· (graphite)	338.0	[76]
	$PdCl_2$· (graphite)	337.9±0.3	[98]
15*	$PdCl_2L_2$ (*trans*)	338.3	[76]
16	K_2PdCl_4	338.4±0.2	[98]
17*	PdI_2L_2 (*trans*)	337.7±0.4	[98]
18*	$Pd(OOCCH_3)_2L_2$	338.1	[95]
19*	$[Pd(OOCCH_3)_2L]_2$	338.5	[95]
20	$PdI_2(CH_3NC)_2$	338.9	[96]
21	$[Pd(OOCCH_3)_2]_n$	338.8	[95]
22	$Pd(CH_3NC)_4(PF_6)_2$	339.5	[96]
23	$Pd(CN)_2$	339.6	[98]
24	$Pd(OOCCF_3)_2$	339.7	[99]
	Pd(IV)		
25	K_2PdCl_6	340.3±0.3	[98]
26	K_2PdF_6	342.8	[100]

*L = $P(C_6H_5)_3$. **Spectra obtained by Yu.G.Borod'ko and T.S.Moravskaya (OIKhF, USSR Academy of Sciences).

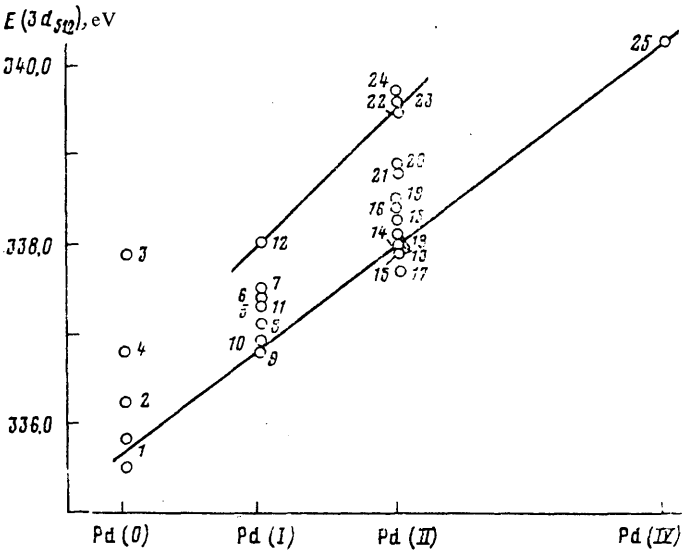


Figure 2. XPE spectra of metallic palladium and palladium compounds; the numbers against the points correspond to the numbers of the compounds in Table 8.

The influence of the ligands on the position of the $E(3d_{5/2})$ level is very strong, for the oxidation states 0 and +1 the range of variation of E as a function of the ligand is on average ~1.5 eV, and for palladium(II) it is as much as 2 eV. The binding energies in complexes with ligands having pronounced π-acceptor properties (Table 8, Nos.12, 22, and 23) increase to a particularly marked extent also in the case of $Pd(OOCCF_3)_2$. The high values of $E(3d_{5/2})$ for complexes Nos.3 and 4 give rise to some doubts—this may be a possible consequence of the oxidation of zerovalent palladium.

The spectrum of PdI_2, obtained by Kumar et al.[98], also deviates from the general pattern of the XPE spectra presented in Fig.2, the value $E(3d_{5/2}) = 336.6 \pm 0.1$ eV for PdI_2 actually lying below the values obtained for palladium(I). A probable explanation is the possible reduction of the surfaces of the PdI_2 specimens on irradiation in the course of the recording of the spectra.

If a line is drawn in Fig.2 through points *1*, *13*, and *25* corresponding to Pd(0), $PdCl_2$ and K_2PdCl_6, then the value of $E(3d_{5/2})$ for the Pd_2Cl_2-graphite complex lies on this line (Table 8, No.9). The values of $E(3d_{5/2})$ for all the remaining compounds lie above this line and below the line drawn through points *12* and *22*, corresponding to $Pd(CNR)_4^{2+}$ and $Pd_2(CNR)_6^{2+}$. Points *2*, *5*, and *15*, which correspond to phosphine-containing zerovalent palladium, palladium(I), and palladium(II) complexes, lie somewhat above the line drawn through points *1*, *9*, *13*, and *25*. We are aware of two studies of palladium carbonyl complexes by XPE spectroscopy. The binding energies $E(3d_{5/2})$ for PdL_3CO [94] and $[Pd(CO)(OOCCH_3)]_4.2CH_3COOH$ [17] are 337.9 and 338.7 eV respectively. The replacement of $P(C_6H_5)_3$ by CO in the complexes PdL_4 (Table 8, No.2) and $Pd_2L_2(OOCCH_3)_2$ (Table 8, No.8) should increase the binding energy $E(3d_{5/2})$ owing to the pronounced π-acceptor properties of the CO group; however, the observed increase of $E(3d_{5/2})$ by 1.6–1.7 eV appears to be very surprising.

Thus the interpretation of the XPE spectroscopic data for the purpose of the identification of palladium(I) complexes should be approached with caution. It is desirable to compare the spectra of complexes with similar sets of ligands or with ligands which have only a slight influence on the electron density of the central atom (Cl, Br, PR_3, CH_3COO, AsR_3).

III. SYNTHESIS AND REACTIONS OF PALLADIUM(I) COMPLEXES

We shall consider the principal methods of synthesis of palladium(I) complexes, their oxidation-reduction properties, and their oxidation-reduction reactions. These problems are mostly inter-related, because the principal difficulties in the synthesis of compounds of palladium in the intermediate +1 oxidation state are due to the capacity of palladium(I) for oxidation, reduction, and disproportionation.

The first palladium(I) complexes were obtained by the reduction of palladium(II) compounds, but at the present time numerous palladium(I) complexes have been synthesised [directly] and information has been obtained about their chemical properties. Ligand substitution reactions are therefore widely used for the synthesis of new palladium(I) compounds.

1. Ligand Substitution Reactions Involving Palladium(I) Complexes

The polymeric carbonyl halides $[Pd(CO)X]_n$ or the dimer $H_2Pd_2(CO)_nCl_4$ in hydrochloric acid solutions are frequently used as the starting compounds. Thus the complexes $Pd_2L_2X_2$ have been synthesised[40] by treating $[Pd(CO)X]_n$ (X = Cl or Br, L = dpm or dam) with the ligand in methylene chloride. The addition of lithium or caesium iodide to the hydrochloric acid solution of $H_2Pd_2(CO)_nCl_4$ leads to the evolution of CO and the formation of the complex $M_2Pd_2I_4.2H_2O$ (M = Li or Cs) [51] (Table 2).

The complexes $[Pd_2X_2L_2]CO$ [45] (Table 2), in which one CO group corresponds to two Pd atoms, have been isolated as a result of the reaction of a hydrochloric acid solution of $P(C_6H_5)_3$ with $H_2Pd_2(CO)_nCl$ using the proportions [L] : [Pd] = 1.5. The ligand substitution reactions involving palladium(I) carbonyl halide complexes may be accompanied by extremely complicated processes. Thus the reaction of $[Pd(CO)Cl]_n$ with dam involve the insertion of CO in the Pd–Pd bond[63] (see below) and the interaction of $H_2Pd_2(CO)_nCl_4$ with MI results in the evolution of small amounts of CO_2 and H_2 together with CO.[51]

The mode of the substitution reaction and the product composition depend on the nature of the substituting ligand, the [L] : [Pd] ratio, and other factors. Thus, when the carbonyl acetate complex $[Pd_2(CO)_2(CH_3COO)_2]_2$ [17–19] was used as the starting material for the synthesis of palladium(I) complexes with other ligands, it was established[44] that unstable complexes are formed for the initial reactant ratio [L] : [Pd] = 0.25, where L = $(C_6H_5)_3$, C_5H_5N, ½ bipy, or ½ phen. For [L] : [Pd] = 0.5, the state of palladium(I) is stabilised by triphenylphosphine 2,2-bipyridyl, and o-phenanthroline. Treatment with pyridine and its alkyl derivatives leads to the evolution of the entire carbon monoxide bound in the initial carbonyl acetate and the precipitation of metallic palladium; palladium(II) complexes are detected in solution.

The substitution reactions are different for different palladium(I)-stabilising ligands. Treatment with $P(C_6H_5)_3$ also leads to the complete evolution of carbon monoxide and the formation of the complex $Pd_2[P(C_6H_5)_3]_2.(CH_3COO)_2$ [44] (Table 2). The composition of the ligand substitution reaction products when o-phenanthroline and bipyridyl are employed is determined by the initial concentrations of these ligands and palladium(I) carbonyl acetate for [L] : [Pd] = 0.5. In bipyridyl solutions at concentrations ≥0.5 M the entire carbon monoxide is evolved:

$$[Pd_2(CO)_2(OOCCH_3)_2]_2 + 2bipy \rightarrow 2Pd_2bipy(CH_3COO)_2 + 4CO.$$

For [bipy] ≤ 0.5 M, half of the carbon monoxide remains in the coordinated form:

$$[Pd_2(CO)_2(OOCCH_3)_2]_2 + 2bipy \rightarrow 2Pd_2(CO)bipy(CH_3COO)_2 + 2CO.$$

Whatever its concentration, phenanthroline displaces half of the CO molecules present in the carbonyl acetate complex:

$$[Pd_2(CO)_2(OOCCH_3)_2]_2 \xrightarrow{[phen]<10^{-2}\ M} 2Pd_2(CO)\,phen\,(CH_3COO)_2 + 2CO;$$
$$[Pd_2(CO)_2(OOCCH_3)_2]_2 \xrightarrow{[phen]\geq 0.5\ M} 2Pd_2(CO)\,phen_2\,(CH_3COO)_2 + 2CO.$$

In the carbonyl complexes with bipyridyl and phenanthroline as ligands, the acetate is reversibly substituted by the anion X (X = ClO_4^-, Cl^-, CCl_3COO^-, CF_3COO^-, or CNS^-).[44]

The ligand and outer anion substitution reactions involving the isonitrile complexes of palladium(I) have been investigated[31,33]. The methylisocyanide groups in the cationic complexes $[(CH_3NC)_6Pd_2]^{2+}$ are exchanged at a high rate with free methyl isocyanide in acetone solution in the temperature range +40– –50 °C. On treatment with an excess of $t\text{-}C_4H_9NC$ or C_6H_5NC under conditions ensuring the removal

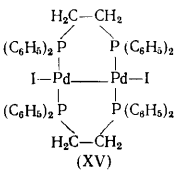
of the methyl isocyanide molecules to be substituted, it is possible to replace completely the methyl isocyanide groups and to isolate the complexes $[(t\text{-}C_4H_9NC)_6Pd_2](PF_6)_2$ and $[(C_6H_5NC)_6Pd_2](PF_6)_2$.[31,33] The same workers obtained complexes containing one or two triphenylphosphine groups (Table 1) in the axial coordination positions. It is not possible to substitute more than two methylisocyanide groups by triphenylphosphine[31,33].

Complexes of the type $[Pd_2(\text{diphosphine})_2(CH_3NC)_2](PF_6)_2$ have been obtained recently§ by the substitution of isonitrile ligands in the complex $[Pd_2(CH_3NC)_6](PF_6)_2$ by the diphosphines $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 2–4) or *cis*-$(C_6H_5)_2PCH=CHP(C_6H_5)_2$. According to NMR data, these complexes have a symmetrical non-bridged structure in which the diphosphine ligand is bound to one palladium atom. When the triphosphine $(C_6H_5)_2P(CH_2)_2P(C_6H_5)(CH_2)_2P(C_6H_5)_2$ is used in an analogous reaction, the isonitrile ligands are fully substituted and crystals of the complex $\{Pd_2[(C_6H_5)_2P(CH_2)_2P(C_6H_5)(CH_2)_2P(C_6H_5)]_2\}(PF_6)_2$ are formed. The absence of reactions of the isonitrile complexes with CO, pyridine, 2,2′-bipyridyl, cyclo-octa-1,5-diene, and tetrachloroethylene has been noted[31-34].

The complexes $Pd_2X_2(CNR)_4$ have been obtained by the substitution of some of the isonitrile groups by the corresponding ligands (X = I or SCN; R = CH_3, t-C_4H_9, or C_6H_5) in the complexes $[Pd_2(RNC)_6](PF_6)_2$.[31,33] The complex $Pd_2I_2(t\text{-}C_4H_9NC)_4$ has been used[30] to synthesise palladium(I) complexes with phosphorus-containing ligands:

$$Pd_2I_2(t\text{-}C_4H_9NC)_4 \xrightarrow{2P(C_6H_5)_3} Pd_2I_2(t\text{-}C_4H_9NC)_2[P(C_6H_5)_3]_2;$$
$$Pd_2I_2(t\text{-}C_4H_9NC)_4 \xrightarrow{[P(C_6H_5)_2CH_2]_2} Pd_2I_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2.$$

Presumably the complex with the diphosphine ligand has structure (XV), analogous to the structure of the complexes with bis(diphenylphosphino)methane[49].

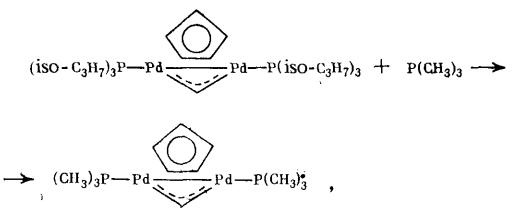


(XV)

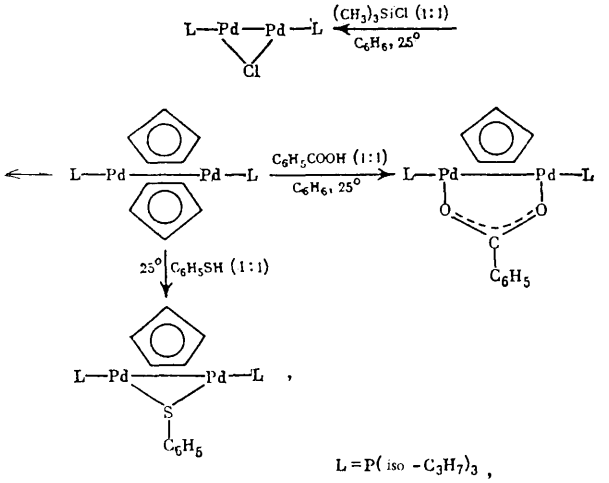
There is virtually no information about substitution reactions involving π-complexes of palladium(I). The possibility of the substitution of the ClO_4^- anion in Davidson's complex has been demonstrated[71]:

$$[Pd(ClO_4)(H_2O)(C_6H_6)]_2 \xrightarrow{H_2SO_4} [Pd_2(C_6H_6)_2](HSO_4)_2.$$

The substituion of a neutral ligand[88],

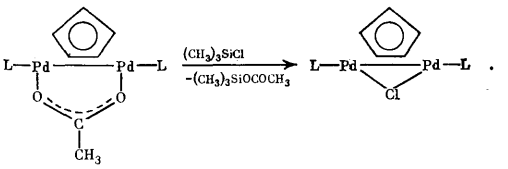


and of a single cyclopentadienyl ligand by Cl^-, $C_6H_5COO^-$, or $C_6H_5S^-$,[85]

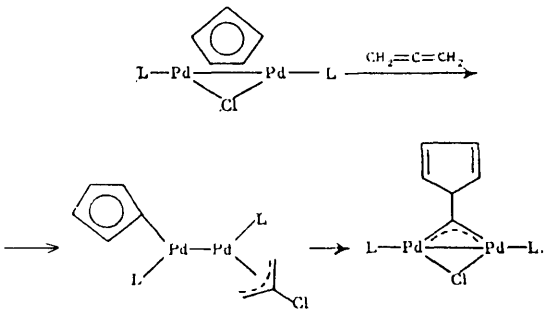


L = P(iso-C_3H_7)$_3$,

has been reported. The acetate ligand in the analogous complex can be substituted by Cl^-:[83]



The only reaction of the π-ligands without change in the oxidation state of palladium(I) has apparently been described by Kühn and Werner[88]:



L = iso-C_3H_7

It follows from the substitution reactions described above that this method of synthesis of palladium(I) complexes is fairly convenient and extremely effective.

2. Synthesis of Palladium(I) Complexes by the Reduction of Palladium(II) Compounds

The reduction of palladium(II) compounds constitutes the most general method of synthesis of palladium(I) complexes. When this reaction is carried out, it is necessary to employ ligands which stabilise the intermediate palladium(I) oxidation state and prevent the disproportionation reaction

$$Pd_2^I \rightarrow Pd^{II} + Pd^0. \qquad (3)$$

In some cases the same substance can fulfill the functions of the reductant and the ligand:

$$Pd^{II} + L(\text{Red}) \rightarrow Pd^IL + L'(\text{Ox}).$$

§C.H.Lindsay, L.S.Benner, and A.L.Balch, Inorg.Chem., 1980, 19, 3503.

CO,[3,40,41] C_6H_6,[70] C_6H_8,[73] and RNC [27,32,34] have been used as such bifunctional reagents. However, this type of combination of functions is not always possible and palladium(I) complexes are therefore usually synthesised in accordance with the equation

$$Pd^{II} + Red + L \rightarrow Pd^{I}L + Ox .$$

The following combinations of reductants and ligands, in which the reductant fulfilled in many instances also the function of an additional ligand, have been used to synthesise π- and σ-complexes: Na/Hg–CN^-,[101] CO–CH_3COO^-,[17–19] Al–C_6H_6,[67,68] CO–phen, CO–bipy,[43,44] H_2–C_6H_6,[71,72] C_6H_{12}–C_6H_6,[71,72] H_2–$P(C_6H_5)_3$,[50] and C_2H_2–I^-, $CrCl_2$–I^-,[51,102] and C_2H_4–*p*-benzoquinone[74]. For example, the bis-π-arene complex of palladium(I) was obtained for the first time by the reaction[67]:

$$2PdCl_2 + 4AlCl_3 + \tfrac{2}{3}Al + 2C_6H_6 \rightarrow Pd_2(C_6H_6)_2(Al_2Cl_7)_2 + \tfrac{2}{3}AlCl_3 .$$

The series of reductants Mg, Na/Hg, LiAlH $(t\text{-}C_4H_9O)_3$, $LiAlH_4$, $NaBH_4$, and $n\text{-}C_4H_9MgBr$ [80,84] have been used to synthesise the complexes $[(\mu\text{-}C_5H_5)(\mu\text{-}X)Pd_2(PR_3)_2]$ (X = Br, R = iso-C_3H_7, C_6H_5, or C_6H_{11}; X = Cl or I, R = iso-C_3H_7). A paramagnetic palladium(I) complex with thiolene ligands is synthesised by the electrochemical reduction of the corresponding palladium(II) compound[8].

One of the possible mechanisms of the formation of palladium(I) complexes with a Pd–Pd bond in the instances enumerated consists in the reaction of the zerovalent palladium complex formed initially with palladium(II), i.e. involves a reaction which is the opposite of the disproportionation reaction (3), for example:

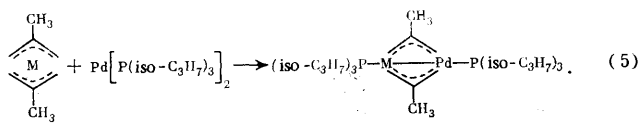
$$\begin{gathered}\tfrac{1}{2}(C_3H_5PdI)_2 + 3P(C_6H_5)_3 \rightarrow [C_3H_5P(C_6H_5)_3]^+I^- + Pd[P(C_6H_5)_3]_2 ;\\ \tfrac{1}{2}(C_3H_5PdI)_2 + Pd[P(C_6H_5)_3]_2 \rightarrow [C_3H_5Pd_2IL_2] ;\\ 2(\pi\text{-}C_6H_5)Pd(2\text{-}CH_3C_3H_4) + 2PR_3 \rightarrow (C_6H_5)Pd_2(2\text{-}CH_3C_3H_4)(PR_3)_2 + C_6H_5C_3H_4CH_3 ;\\ L = P(C_6H_5)_3 .\end{gathered} \quad (4)$$

The compound $[C_3H_5P(C_6H_5)_3]^+I^-$ has been isolated[79].

The possibility of reactions of this type has been demonstrated by direct synthesis of palladium(I) complexes from palladium(II) and zerovalent palladium complexes. Thus the isonitrile complexes of palladium(I) of the type $Pd_2X_2(t\text{-}C_4H_9NC)_4$ have been obtained by the reaction of $Pd(t\text{-}C_4H_9NC)_2$ with $PdX_2(t\text{-}C_4H_9NC)_2$ (X = Cl, Br or I) at −30 °C in chlorobenzene[30]. Analogous complexes have been prepared from $PdCl_2(C_6H_5NC)_2$ and $Pd(dba)_n$¶ (*n* = 2 or 3) in the presence of an excess of the isonitrile[32]. The reaction of platinum(II) and zerovalent palladium complexes results in the formation of compounds containing the Pt–Pd fragment[26,29]:

$$2[(CH_3NC)_4Pt][PF_6]_2 + Pd_2(dba)_3\cdot CHCl_3 \xrightarrow[CH_3NC]{CH_3CN} 2[(CH_3NC)_6PdPt][PF_6]_2 .$$

The complex $Pd_2[P(C_6H_5)_3]_2(CH_3COO)_2$ has been synthesised by the reaction of $Pd_2[P(C_6H_5)_3]_2$ with $[(C_6H_5)_3PPd\cdot(CH_3COO)_2]_2$.[50] Numerous π-complexes with cyclopentadienyl and allyl ligands have been obtained in accordance with the same scheme (Table 7), for example:



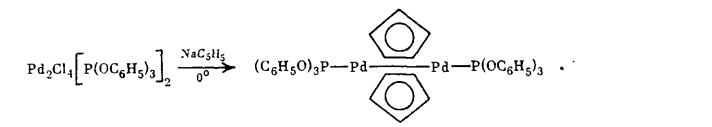
(5)

The coordination-unsaturated zerovalent palladium complex of the type PdL_2 or the zerovalent palladium complex $Pd_m(dba)_n$ which readily loses ligands is involved in reactions via Scheme (5). It is therefore extremely important to follow the ratio L/Pd in the syntheses of complexes with π-allyl and π-cyclopentadienyl ligands. Thus, when L/Pd > 4, the complex PdL_4 is formed instead of the palladium(I) complexes [reaction (4)].

Owing to the absence of the complex $Pd(C_5H_5)_2$, the bis-cyclopentadienylpalladium(I) complex has to be synthesised by a more complicated procedure[85]:

$$\begin{gathered}Pd_2Cl_2L_2(\mu\text{-}OOCCH_3)_2 \xrightarrow{TlC_5H_5} 2C_6H_5PdL(OOCCH_3) \rightarrow\\ \xrightarrow[C_6H_6]{NaK_{2.8}} Pd_2(\mu\text{-}C_5H_5)_2L_2 ;\\ L = P(iso\text{-}C_3H_7)_3 .\end{gathered}$$

An analogous complex has also been obtained via the reaction[89]



The reactions of zerovalent palladium and palladium(II) complexes have been used to synthesise palladium(I) dimers fixed on the surface of silica gel[64]:

$$\boxed{Si}-P_2Pd(OOCCH_3)_2 \xrightarrow{Red} \boxed{Si}-P_2Pd \xrightarrow{Pd(CH_3COO)_2} \boxed{Si}-P_2Pd_2(OOCCH_3)_2$$

where $\boxed{Si}-P_2$ is silica gel with grafted groups containing tertiary phosphines and Red is formic acid.

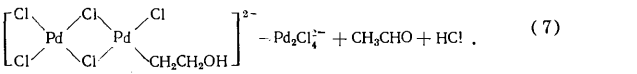
Other mechanisms of the formation of palladium(I), involving the reactions of hydride and σ-organopalladium intermediates, are also possible[102]:

$$HPdX + PdX_2 \rightarrow HX + Pd_2X_2 .$$

This mechanism probably operates in the reduction of palladium(II) with carbon monoxide, acetylene, and alcohol[103], as well as hydrogen[71], and in other reactions leading to the appearance of hydride complexes:

$$RPdX + PdX_2 \rightarrow \begin{cases} \rightarrow RX + Pd_2X_2 \\ \rightarrow R_{-H} + Pd_2X_2 + HX . \end{cases} \quad (6)$$

This mechanism, involving the oxidative demetallation of RPdX, does not include a stage in which zerovalent palladium is formed. The demetallation of a dimeric σ-organopalladium compound and the formation of palladium(I) in the oxidation of olefins by palladium(II) chloride probably take place in precisely this manner[104]:



(7)

3. The Oxidation-Reduction Properties and Reactions of Palladium(I) Complexes

As already mentioned above, palladium(I) complexes exhibit in their reactions the properties of both reductants and oxidants, which is reflected primarily in the disproportionation reaction (3), which is very characteristic of palladium(I). The ligand coordinated to palladium(I) or a nucleophile interacting with the coordinated ligand (CH_3COO^-, RO^-, H_2O, ROH) can play the role of the reductant. Thus on heating to 70 °C *in vacuo*, the complex $Pd_2(C_6H_8)(OOCCH_3)_2$ undergoes the reaction[73]

$$Pd_2(C_6H_8)(OOCCH_3)_2 \rightarrow 2Pd_{met} + C_6H_6 + 2CH_3COOH .$$

¶ Here and henceforth dba = dibenzylideneacetone.

The reaction of the complex $[Pd_2(CO)_2(OOCCH_3)_2]_2$ in the presence of CH_3COONa in acetic acid at 90 °C is of interest[105]:

$$Pd_2(CO)_2(OOCCH_3)_2 \xrightarrow{CH_3COONa} 2Pd_{met} + CO_2 + (CH_3CO)_2O \,. \qquad (8)$$

The probable mechanism of reaction (8) involves attack by the acetate ion on the coordinated carbon monoxide[105]:

$$Pd_2(CO)_2(OOCCH_3)_2 + CH_3COO^- \rightarrow Pd_2(CO)(OOCCH_3)_2(\overset{\overset{O}{\|}}{COOCCH_3})^- \rightarrow$$

$$\xrightarrow{-CO_2} Pd_2(CO)(OOCCH_3)_2(\overset{\overset{O}{\|}}{CCH_3})^- \rightarrow 2Pd_{met} + CO + CH_3COO^- + (CH_3CO)_2O \,.$$

As already mentioned above, palladium(I) carbonyl halides are readily reduced by H_2O. Thus treatment of $[Pd(CO)Cl]_n$ [$\nu(CO)$ = 1975, 1930 cm^{-1}] with water leads to the slow formation of CO_2 and metallic palladium[106]. The rate of formation of CO_2 increases sharply following the addition of $Cr_2O_7^{2-}$ or *p*-benzoquinone in an acid medium[106]. The same palladium(I) carbonyl in methanol or in methanol containing CH_3ONa gives rise to $ClCOOCH_3$, i.e. the product of the reductive elimination reaction[107]:

$$ClPd{-}PdCOOCH_3 \rightarrow 2Pd_{met} + ClCOOCH_3 \,.$$

This mechanism has been confirmed by the following reaction[107]:

$$\frac{2}{n}[Pd(CO)Cl]_n + CH_3COOHgCOOCH_3 \rightarrow [Pd_2(COOCH_3)Cl(CO)_2] \rightarrow$$

$$\rightarrow ClCOOCH_3 + 2Pd_{met} + 2CO + Cl^- \,.$$

In the decomposition of $[Pd(CO)Cl]_n$ in alcohol in the presence of *p*-benzoquinone, the reaction pathway changes and dimethyl oxalate is mainly formed[107]. Treatment of $[Pd_2(CO)_2(OOCCH_3)_2]_2$ with water and ethanol also leads to the formation of CO_2 and the product of the oxidative carbonylation of methanol, namely dimethyl carbonate[105].

The behaviour of palladium(I) complexes with respect to a reductant such as H_2 depends greatly on the nature of the ligands. For example, the reduction of the palladium(I) acetate complex[50] leads to the formation of the diamagnetic cluster Pd_2L_2:

$$Pd_2(OOCCH_3)_2L_2 + H_2 \rightarrow Pd_2L_2 + 2CH_3COOH \,,$$

while the compounds $Pd_2(C_6H_6)_2(HSO_4)_2$ and $Pd_2(CH_3NC)_6 \cdot (PF_6)_2$ are not reduced by hydrogen.

Palladium(I) in complexes is oxidised by various oxidants (O_2, I_2, Br_2, MnO_4^-, $Cr_2O_7^{2-}$, *p* benzoquinone, etc.), including coordinated ligands, for example NO:[47]

$$2Pd(NO)Cl + 8CN^- + H_2O \rightarrow 2Pd(CN)_4^{2-} + N_2O + 2Cl^- + 2OH^- \,.$$

The quantitative characteristics of the oxidation-reduction properties have so far been obtained only for several palladium(I) complexes, but extensive experimental data have been accumulated on reactions of the oxidation-reduction type which it would be useful to analyse and to estimate at least approximately the oxidation-reduction properties of palladium(I). For this purpose, we shall consider in greater detail the disproportionation reaction

$$Pd_2^I \rightleftarrows Pd^0 + Pd^{II} \,.$$

The complexes $Pd_2(C_6H_6)_2^{2+}$ do not disproportionate in acetic and sulphuric acid solutions and only the addition of Cl^- leads to a rapid oxidation-reduction process. This finding is in good agreement with the hypothesis[108,109] that $Pd_2Cl_4^{2-}$, formed via reaction (7), tends to disproportionate in accordance with the mechanism

$$Pd_2Cl_4^{2-} \rightleftarrows Pd_{met} + PdCl_4^{2-} \,. \qquad (9)$$

It can be easily shown that the free energy ΔG° of reaction (9) is negative if the standard oxidation-reduction potentials ε_2^0 and ε_1^0 in the scheme below

$$PdCl_4^{2-} \xrightarrow{\varepsilon_1^0} \tfrac{1}{2}Pd_2Cl_4^{2-} \xrightarrow{\varepsilon_2^0} Pd_{met} \qquad (10)$$

$$\varepsilon_3$$

satisfy the inequality $\varepsilon_2^0 > \varepsilon_1^0$. In this case $\varepsilon_1^0 < 0.62$ V and $\varepsilon_2^0 > 0.62$ V when $\varepsilon_3^0 = 0.62$ V.[110] Since according to some data[108,109] *p*-benzoquinone (Q) oxidises $Pd_2Cl_4^{2-}$ in acid media and the potential of benzoquinone ε_Q varies from 0.7 to 0.6 V in the pH range 0–2, one may conclude that ε_1^0 is indeed smaller than 0.6 V. If it is assumed that the reaction of the palladium(I) complex with an oxidant (Ox) reaches equilibrium[11],

$$Pd_2^I + Ox \rightleftarrows 2Pd^{II} + Red \,, \qquad (11)$$

it is possible to achieve a further refinement of the values of ε_1^0 and ε_2^0. Since the expression for ε_1^0 corresponding to reaction (11) assumes the form (in terms of the concentration approximation)

$$\varepsilon_1^0 = \varepsilon_{Ox/Red}^0 - \frac{RT}{2F}\ln\frac{[Red][Pd^{II}]^2}{[Ox][Pd_2^I]} \,, \qquad (12)$$

it is possible to estimate Δ in Eqns.(12) and (13) by specifying different degrees of conversion of $Pd_2(I)$ and using the real concentrations of all the components:

$$\varepsilon_1^0 = \varepsilon_{Ox/Red}^0 - \Delta \,. \qquad (13)$$

In the calculation of Δ it is of course necessary to take into account the concentration of H^+ ions and the ligands involved in the reaction (11). When account is taken of Δ (estimated from the data of Moiseev and Pestrikov[108]), the potential ε_1^0 for $Pd_2Cl_4^{2-}$ can be $\varepsilon_1^0 \leqslant 0.5$ V; then $\varepsilon_2^0 \geqslant 0.74$ V.

The complex $Pd_2SO_4 \cdot Q$ [74] is formed in an acid medium with $[H^+] = 0.1$–0.2 M. Since metallic palladium cannot be oxidised by *p*-benzoquinone to $PdSO_4$ in sulphuric acid solutions[110], one may assume that metallic palladium is oxidised to Pd_2SO_4, which is additionally stabilised by *p*-benzoquinone:

$$2Pd_{met} + 2Q + H_2SO_4 \rightarrow Pd_2SO_4 \cdot Q + QH_2 \,.$$

Hence, without taking into account the complex formation reaction of Q with Pd_2SO_4, we obtain $\varepsilon_2 \leqslant 0.7$ V [the designation of the potentials is analogous to that in scheme (10)]. If it is assumed that ε_3^0 for $PdSO_4/Pd_{met}$ does not differ greatly from $\varepsilon^0_{Pd^{2+}/Pd_{met}} = 0.987$ V,[110] we obtain $\varepsilon_1^0 \geqslant 1.1$ V (for $HgSO_4$, $\varepsilon_1^0 = 0.92$ V and $\varepsilon_2^0 = 0.789$ V). The complex $Pd_2SO_4 \cdot Q$ does not disproportionate precisely because in this case $\varepsilon_2^0 < \varepsilon_1^0$ and in addition there is a possibility of some stabilisation of palladium(I) on treatment with *p*-benzoquinone. The addition of concentrated hydrochloric acid to $Pd_2SO_4 \cdot Q$ leads immediately to the oxidation of palladium(I) and the formation of hydroquinone and $PdCl_4^{2-}$ (because Cl^- displaces Q and SO_4^{2-} from the coordination sphere of palladium and lowers ε_1^0).[74]

The complex $Pd_2(C_6H_6)_2(ClO_4)_2$ [70] is oxidised by O_2, Br_2, and $KMnO_4$. However, $Cr_2O_7^{2-}$ and $Pb(OCOCH_3)_4$ in acetic acid oxidise this complex only in the presence of Cl^-. The high potential of $Cr_2O_7^{2-}$ in the six-electron reduction ($\varepsilon^0_{Ox/Red} = 1.33$ V) in a weakly acid medium is probably low in the first stages of the oxidation [Cr(VI) → Cr(V) → Cr(IV)] and for this reason $Cr_2O_7^{2-}$ does not oxidise the stabilised cation $Pd_2(C_6H_6)_2^{2+}$ in the absence of Cl^-; only in concentrated 90% H_2SO_4 is that cation oxidised by dichromate[74].

The complex $Li_2Pd_2I_4 \cdot 2H_2O$ in butanol is oxidised by I_2.[51] In the presence of an excess of LiI, at a concentration of 0.5 M for $[Pd_2^I] = 0.01$ M, the complex probably exists in

the form $Pd_2I_6^{4-}$. In this case the oxidation reaction can be formulated as the equilibrium

$$Pd_2I_6^{4-} + I_2 \rightleftarrows 2PdI_4^{2-}. \qquad (14)$$

The standard potentials of the I_2/I^- and I_3^-/I^- pairs in water are 0.62 and 0.55 V [$\varepsilon^0_{Ox/Red}$ in Eqns.(12) and (13)]. Judging from potentiometric data[97], equilibrium (14) is almost completely displaced to the right. For a degree of conversion of PdI_2 of 0.99 and at the real concentrations of the reactants, $\Delta = 0.15$ V in Eqn.(13). If it is assumed that in butanol $\varepsilon^0_{Ox/Red}$ for I_2 does not differ greatly from the value in aqueous solutions and amounts to ~0.6 V, then ε_1^0 in scheme (15) is $\varepsilon_1^0 \leqslant 0.45$ V†:

$$\begin{array}{ccccc} PdI_4^{2-} & \xrightarrow{\varepsilon_1^0} & \tfrac{1}{2}Pd_2I_6^{4-} & \xrightarrow{\varepsilon_2^0} & Pd^0_{met} \\ & \searrow^{\varepsilon_3^0} & & \nearrow & \end{array} \qquad (15)$$

According to Fasman[111], the overall instability constant of the complex PdI_4^{2-} in water at $I = 1$ is close to 10^{-24}. Then (on the same assumptions) $\varepsilon_3^0 \cong 0.3$ V and $\varepsilon_2^0 \geqslant 0.15$ V. The above estimate makes it possible to explain the stability of the palladium(I) iodide complex with respect to the disproportionation reaction ($\varepsilon_2^0 < \varepsilon_1^0$). The potentials of system (15) are probably very similar to those of the system $HgBr_4^{2-} \rightarrow \frac{1}{2}Hg_2Br_2 \rightarrow Hg^0$ [110] ($K_{inst} = 2.3 \times 10^{-22}$, $\varepsilon_1^0 = 0.31$ V, $\varepsilon_2^0 = 0.14$ V, and $\varepsilon_3^0 = 0.227$ V).

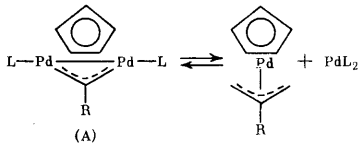
The complex $Pd_2(CH_3NC)_6^{2+}$ proved to be very stable with respect to oxidants. It is not oxidised by O_2 and chloranil[34], but is oxidised by iodine (and bromine) via the reaction

$$Pd_2L_6^{2+} + I_2 \rightarrow PdL_4^{2+} + PdI_2L_2.$$

Here I_2 in essence displaces the disproportionation equilibrium to the right:

$$PdL_2^0 + I_2 \rightleftarrows PdI_2L_2.$$

The disproportionation reaction proceeds also in the case of π-cyclopentadienyl-π-allyl complexes[88]. Thus the equilibrium in the reaction



(A)

is usually strongly displaced to the left (see Section III, subsection 2 above), but is displaced to the right in the presence of substituents giving rise to an appreciable steric hindrance (R = t-C_4H_9 and L = PR_3). The complexes (A) are readily oxidised by I_2, CH_3I, and even HCl, but in this instance the primary reaction products are those resulting from the oxidative addition of I_2 and CH_3I (as well as HCl) to PdL_2^0:[80]

$$(A) + I_2 \rightarrow [(C_6H_5)Pd(R - C_3H_4) + L_2PdI_2] \rightarrow (C_6H_5)PdLI + (R - C_3H_4)PdLI.$$

In conclusion of this Section, we shall consider the results of polarographic studies of palladium(II) and palladium(I) complexes. The number of studies devoted to the polarography of palladium(II) is small. At a mercury electrode, polarographic waves can be detected for complexes whose oxidation potential ε^0 is in excess of 0.25 V [i.e. above the potential of the saturated calomel electrode (s.c.e.)].[112] The measured values of $E_{\frac{1}{2}}$ for palladium(II) are therefore in the range between −0.3 and −1.96 V (relative to s.c.e.) or in the range −0.05– −1.65 V (relative to the hydrogen electrode). Thus the $E_{\frac{1}{2}}$ refer to complexes in which the state of palladium(II) is much more stable than the zerovalent palladium and palladium(I) states [C_5H_5N, NH_3, $P(OR)_3$, dpe, CN^-, acac$^-$, $S_2C_2(CN)_2^{2-}$].[8,112–116]#

Polarographic studies of palladium(II) cyanide complexes[113] yielded for the first time the electrochemical characteristics of the palladium(I) cyanide complex. The value of $E_{\frac{1}{2}}$ (relative to s.c.e.) for the reaction $Pd(CN)_4^{2-} + 2e \rightarrow Pd(CN)_4^{4-}$ is −1.6 V (reversible reaction). The product of the dimerisation of $Pd(CN)_4^{3-}$, namely $Pd_2(CN)_6^{4-}$, does not give rise to a cathodic wave. The anodic half-wave potential of this intermediate (−0.85 V) is close to the anodic half-wave potential of the product of the reduction of $Pd(CN)_4^{2-}$ by sodium amalgam (−0.93 V). In order to estimate ε_1^0 for the transition $Pd(CN)_4^{2-} \rightarrow \frac{1}{2}Pd_2(CN)_6^{4-}$ from the potential of the anodic wave, we shall assume that the transition is reversible. Then $\varepsilon_1^0 = -0.65$ V (relative to the hydrogen electrode). Using the value $K_{inst} = 10^{-51}$ for $Pd(CN)_4^{2-}$,[111] we obtain $\varepsilon_3^0 = -0.51$ V and $\varepsilon_2^0 = -0.38$ V. It follows from these estimates that CN^- stabilises palladium(II) to a much greater extent than zerovalent palladium and palladium(I) and the postulated complex $Pd_2(CN)_6^{4-}$ is therefore a very powerful reductant. The half-wave potential of the reversible cathodic Pd(II)/Pd(I) transition was first measured with a dithiolenepalladium(II) complex[8]. The reaction

$$Pd(mnt)_2^{2-} + e \rightleftarrows Pd(mnt)_2^{3-} \qquad (16)$$

where mnt = $(NC)_2C_2S_2^{2-}$, in acetonitrile leads to the formation of the only known paramagnetic palladium(I) (d^9) complex. The complex is stable in acetonitrile and dimethoxyethane and is not reduced further up to a potential of −2.8 V. The value of $E_{\frac{1}{2}}$ for reaction (16) is −1.9 V relative to the aqueous saturated calomel electrode. After a number of assumptions have been made, $\varepsilon^0_{Pd(II)/Pd(I)}$ for this complex is in the range between −1.6 and −1.65 V. Thus the above palladium(I) complex is an exceptionally powerful reductant.

The formation of univalent palladium has been detected also in the polarographic reduction of palladium(II) oxinate and acetylacetonate complexes in DMF.[115] The complexes $Pd(oxine)_2$§ and $Pd(acac)_2$ are reduced in two one-electron stages. In the case of $Pd(oxine)_2$, the potential $E_{\frac{1}{2}}$[Pd(II)/. .Pd(I)] (relative to s.c.e.) corresponds to a reversible reaction and amounts to −1.46 V. The lifetime of palladium(I) is ~0.18 s, the first stage in the reduction of $Pd(acac)_2$ is not fully reversible ($E_{\frac{1}{2}} = -1.29$ V), and the palladium(I) complex decomposes faster (lifetime ~0.02 s).

The first oscillopolarographic characteristics of palladium(I) complexes have been obtained recently in a saturated solution of KCl in 98% acetic acid[46,117]. The complex $K_2Pd_2(CO)_2Cl_4$ has a cathodic reduction potential $E_1 = -0.576$ V (relative to s.c.e.). The complexes $(PdXL)_2CO$ in acetic acid have similar potentials[46,117]. Their electrochemical behaviour has been studied by cyclic voltamperometry[46,117] in DMF and acetonitrile. The reduction potentials of the complexes $(PdXL)_2CO$, reversible in DMF, are in the range −0.56 to −0.63 V (relative to the aqueous hydrogen electrode).

Table 9 presents the values of ε_1^0 and ε_2^0 which we estimated (see above) from indirect or polarographic data or they were measured polarographically. Evidently the oxidation-reduction properties of palladium(I) vary within very wide limits as a function of the nature of the ligands.

†Presumably the equilibrium constant of $PdI_3^- + I^- \rightleftharpoons PdI_4^{2-}$ is small and does not alter ε_1^0 appreciably.

#Here and henceforth acac$^-$ = acetylacetonate anion.

§Oxine = 8-hydroxyquinolinate anion.

4. Reactions Involving the Insertion of Various Molecules in a Pd–Pd Bond

The first complex containing a CO molecule inserted in a Pd–Pd bond was synthesised in 1973,[40] but its structure was interpreted erroneously. The diamagnetic complex $Pd_2dam_2.Cl_2(CO)$ was obtained by the reaction[40,63]

$$\frac{2}{n}(PdCOCl)_n + 2\,dam \rightarrow Pd_2(dam)_2Cl_2(CO) + CO\ .$$

Table 9. Estimated standard potentials for palladium(I) complexes [the notation is based on Scheme (10)].

Complex	Solvent	ε^0_1, V	ε^0_2, V
$Pd_2SO_4 \cdot Q$	water	$\geqslant 1.1$	$\leqslant 0.7$
$Pd_2Cl_4^{2-}$	water	$\leqslant 0.5$	$\geqslant 0.74$
$Pd_2I_6^{4-}$	n-butyl alcohol	$\leqslant 0.45$	$\geqslant 0.15$
$[PdX(PR_3)]_2CO$ *	CH_3CN, DMF	−0.56 – −0.63	—
$Pd(CN)_6^{4-}$ *	water	−0.65 **	−0.38
$Pd(oxine)_2^-$ *	DMF	−1.21	—
$Pd[S_2C_2(CN)_2]_2^{3-}$ *	CH_3CN	−1.6 – −1.65	—

*The potentials relative to the aqueous hydrogen electrode are quoted.

**$\varepsilon^0_1 \cong \varepsilon_{1/2}$.

The surprisingly low vibration frequency of the carbonyl group [$\nu(CO) = 1720\ cm^{-1}$] was explained with the aid of X-ray diffraction analysis[63]. Thus the parameters of a fragment of complex No.1 (Table 10 and Fig.3) indicate the absence of a metal–metal bond. The Pd–C–Pd angle appreciably exceeds the angles in metal carbonyls having the M–C–O–M bridge (<88°) and even in aldehydes and ketones (108–113°).

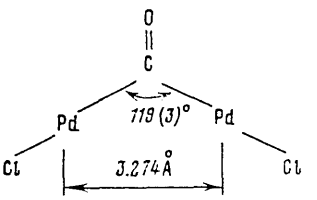


Figure 3. Fragment of the complex $Pd_2(dam)_2Cl_2(\mu\text{-}CO)$.[63]

If the complex $Pd_2dpm_2X_2$ is kept in methylene chloride at p_{CO} = 1 atm, a red crystalline product $(Pd_2dpm_2X_2)CO$ (X = Cl or Br), for which $\nu(CO) = 1704\ cm^{-1}$ when X = Cl, is formed[118]. The RNC molecule behaves similarly to carbon monoxide[118,119] (Table 10), being inserted in the Pd–Pd bond in the following reactions:

$$Pd_2(dpm)_2X_2 + RNC \rightarrow Pd_2(dpm)_2X_2(\mu\text{-}RNC);$$
$$Pd_2(RNC)_6(PF_6)_2 + 2\,dpm \xrightarrow{-3RNC} [Pd_2(dpm)_2(RNC)_2(\mu\text{-}RNC)](PF_6)_2\ .$$
(XVI)

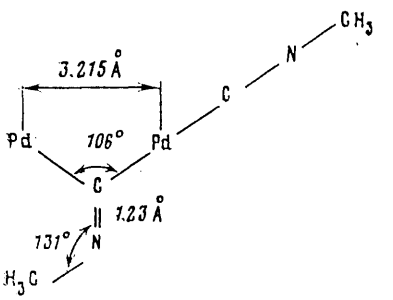


Figure 4. Fragment of the complex $Pd_2(dpm)_2(\mu\text{-}CH_3NC).(CH_3NC)_2(PF_6)_2$.[118]

The stretching vibration frequency of the CN bridge group (μ-RNC) (1640–1680 cm^{-1}) is appreciably reduced compared with that of the terminal ligand (2183–2231 cm^{-1}). The fragment of complex (XVI) (Fig.4) has parameters analogous to those of the fragment of the complex with an inserted CO group, although the Pd–C–Pd angle is appreciably smaller. The products of insertion in a Pd–Pd bond have also been isolated in the case of SO_2 molecules[120], ArN_2^+,[121] alkynes[122], and atomic sulphur[123] (Table 10).

Table 10. Products of the insertion of molecules in a Pd–Pd bond.

Y	L–L	X	L′	$^1_{Pd-Pd}$	References
		$Pd_2(L—L)_2(\mu\text{-}Y)X_2$			
CO	dam	Cl	—	3,274 (8)	[40,63]
CO	dpm	Cl, Br	—	—	[118]
CO	dpm	I, SCN, NCO, N_3	—	—	[119]
SO_2	dpm	Cl	—	3,383 (2)	[120]
SO_2	dpm	Br	—	3,221 (2)	[120]
SO_2	dam	Cl	—	—	[120]
$C_2(CF_3)_2$	dpm	Cl	—	3,492 (1)	[122]
$C_2(COOCH_3)_2$	dpm	Cl	—	—	[122]
S	dpm	Cl	—	—	[123]
CH_3NC, C_6H_5NC, $p\text{-}CH_3C_6H_4NC$	dpm	Cl, Br	—	—	[118]
$C_6H_{11}NC$, CH_3NC	dpm	I, SCN, NCO, N_3	—	—	[119]
		$Pd_2(L—L)_2(\mu\text{-}Y)L_2'X_2$			
CH_3NC	dpm	PF_6	CH_3NC	3,215 (2)	[118]
$p\text{-}CH_3C_6H_4NC$	dpm	PF_6	$p\text{-}CH_3—C_6H_4$	—	[118]
		$Pd_2(L—L)_2(\mu\text{-}Y)L'X_2$			
CH_3NC	dpm	I, SCN	CH_3NC	—	[119]

CO and SO_2 molecules are inserted reversibly while RNC, S, and RN_2^+ are inserted irreversibly. A somewhat idealised structure of all the complexes with an iserted group Y is illustrated in Fig.5. The environment of the Pd atom is planar and almost square. Only in the case of $C_2(CF_3)_2$ does the C–Pd–C angle (~165°) differ appreciably from 180°.

The marked reduction of the ν(CO) and ν(NC) frequencies, the absence of the Pd–Pd interaction, the change in the hybridisation of the carbon atom in the CO, RNC, and C_2R_2 complexes (for example, the C–C=C angles[122] are 122.8° and 124.7°), and the increase in the length of the N=C bonds in RNC and of the C=C bonds in C_2R_2 are all facts indicating that the oxidative addition of various molecules and atoms to palladium(I) complexes takes place via the dissociation of the Pd–Pd bond. Thus the formation of a disubstituted palladium(II) sulphide takes place in essence in the reaction

$$(dpm)_2Pd_2Cl_2 + {}^1/_8S_8 \rightarrow S(PdCl)_2(dpm)_2\ .$$

In the reaction involving CO the characteristics of the inserted carbon monoxide approach those of the carbonyl group in ketones and it is therefore entirely appropriate to regard these complexes as derivatives of dimetallated formaldehyde[124]. Naturally the insertion of C_2R_2 molecules as well as those of $C_2(CN)_4$ and CS_2 [122] in the Pd–Pd bond is an oxidative addition reaction. The reaction involving the insertion of alkenes in an M–M bond is known for nickel(I), cobalt(II), zerovalent cobalt, and molybdenum(I) complexes.

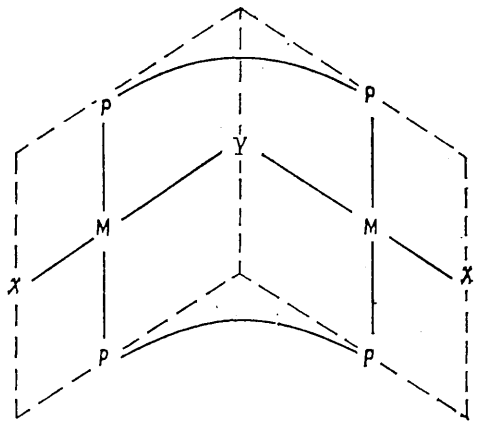


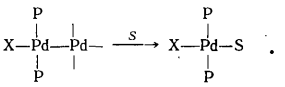
Figure 5. Idealised structure of complexes containing the M–Y–M fragment.

However, studies of the XPE spectra of palladium(I) complexes and the products of the insertion of various molecules have shown[96] that it is impossible to detect appreciable charge transfer and changes in the degree of oxidation of the palladium atoms. This factor led Balch et al.[122] to the conclusion that the question of the degree of oxidation of palladium and of the type of insertion reaction is to a large extent semantic. We shall consider this problem in greater detail. In all cases where it has been possible to measure the binding energy of the electrons at the atom linked directly to two palladium atoms, there is an entirely appreciable decrease of the binding energy on passing from a free to an inserted species. Thus $E(2p_{3/2}) = 161.6$ eV for the S atom in the complex $S(PdCl)_2(dpm)_2$ is lower by 2.4 eV than $E(2p_{3/2})$ for S_8. The transition from free SO_2 to μ-SO_2 decreases the $2p_{3/2}$ binding energy for sulphur by 1.4 to 1.5 eV. Thus there is partial charge transfer to the sulphur atoms. The slight change in $E(3d_{5/2})$ for palladium atoms is also entirely explicable:

(a) electron density is transferred to the inserted species (μ-Y) from two palladium atoms, which decreases the absolute magnitude of the effect;

(b) apart from the two palladium atoms, four (!) powerful σ-donor ligands (P and As) atoms are involved in the charge transfer;

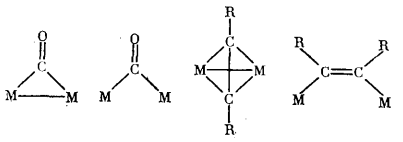
(c) the $3d_{5/2}$ binding energy for palladium (see Section II, subsection 3) depends greatly on the ligand environment (within the limits of 1 eV and more for a constant degree of oxidation). There is therefore a possibility of the mutual cancelling of two effects—the increase of E on transition to palladium(II) and its decrease on transition from the palladium atom as the ligand to, for example, a sulphur atom or CO and SO_2 molecules:



The solution of this problem still requires further study.

The achievement of extremely interesting reactions involving the insertion of various molecules in a Pd–Pd bond expands our ideas concerning the nature of the possible intermediates in catalytic and stoichiometric reactions.

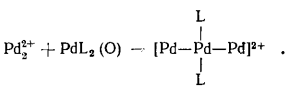
On the basis of the data described above, the types of coordination of CO and acetylenes at the two metal atoms in palladium and platinum complexes can be represented by structures (B), (C), (D), and (E):



(B) (C) (D) (E)

In the case of platinum, a type (C) complex is formed from $Pt_2Cl_2(dpm)_2$ and CO in dichloromethane [ν(CO) = 1638 cm^{-1}] [125–127] and also from the complex $Pt_2(CO)_2Cl_4^{2-}$ and dpm.[125–127]

Within the framework of this Section, which is devoted to reactions involving insertion in a Pd–Pd bond, mention should be made also of the insertion of the PdL_2 complex[11], which can be called a "reductive" addition reaction:



The formal degree of oxidation of palladium approaches +2/3 in this instance.

Thus the Pd–Pd bond in palladium(I) complexes is able to react with both electron acceptors (oxidants—for example, sulphur) and with electron donors (reductants—for example, zerovalent palladium).

IV. THE ROLE OF PALLADIUM(I) COMPOUNDS IN STOICHIOMETRIC AND CATALYTIC REACTIONS

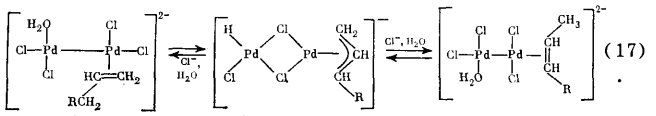
As already mentioned above, the increase of interest in palladium(I) complexes is associated to a large extent with the acquisition of information concerning the involvement of palladium(I) compounds in stoichiometric and catalytic reactions as catalysts and intermediates or about the formation of reaction products containing palladium(I). In this Section we shall consider the available data on the functions of palladium(I) complexes in various reactions. We believe it is useful to mention also the studies in which the postulates of the involvement of palladium(I) are merely working hypotheses and have not yet been sufficiently convincingly demonstrated.

1. The Positional Isomerisation of Olefins

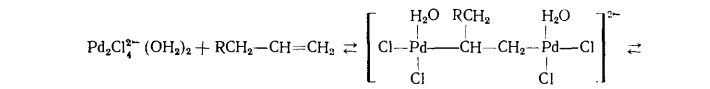
The isomerisation of olefins was apparently the first reaction the results of the study of which were quite convincingly interpreted within the framework of the mechanism of an unbranched chain reaction with a palladium(I) complex as the chain carrier (the catalyst of the isomerisation stages).[104,108,109]. This reaction has been recently discussed in detail[128,129] and we shall therefore mention only its principal features. As a result of the oxidation of an olefin (butenes) with

palladium(II) chloride, a palladium complex is formed [tentatively $Pd_2Cl_4^{2-}$: reaction of type (7)] and catalyses the isomerisation of butenes (α-$C_4H_8 \rightarrow \beta$-C_4H_8). As a consequence of its instability, the complex $Pd_2Cl_4^{2-}$ disproportionates (Section III, subsection 3), which terminates the kinetic chain. The chain termination occurs also after the addition of *p*-benzoquinone (Q), which oxidises palladium(I).[108] Within the framework of this mechanism, it was possible to explain the surprising proportionality of the rate of isomerisation of α-C_4H_8 to its concentration and the concentration of the total olefins $[C_4H_8]_\Sigma$. These results constitute kinetic proof that the isomerisation of olefins is catalysed by a palladium(I) compound. It has been shown[39] that the insoluble palladium carbonyl chloride $[Pd(CO)Cl]_n$ catalyses the isomerisation of liquid hept-1-ene to *cis,trans*-hept-2-enes. These experiments were repeated under homogeneous conditions[51]. The complex $[Pd(CO)Cl]_n$ was synthesised by the method of Kushnikov et al.[38] and was dissolved in DMF saturated with LiCl. The isomerisation of but-1-ene takes place at 20 °C without an inductive period, comes to a complete stop after the addition of *p*-benzoquinone in amounts comparable to those of palladium(I), and is resumed after the reduction of *p*-benzoquinone. It has been shown quite recently[69] that aromatic π-complexes of palladium(I) catalyse the isomerisation of butenes, pentenes, and hexenes at a high rate at room temperature without an inductive period and the hypothesis put forward by Moiseev and co-workers[108,109] has been thereby confirmed.

The mechanism of the isomerisation in the presence of palladium(I) complexes is based on the hypothesis of the transformation of the π-allyl complex, formed as a result of the oxidative addition of $H_2C = CH-CH_2R$ to the complex $Pd_2Cl_4^{2-}$ with dissociation of a C–H bond[104,109]:


(17)

The existence of the dimeric allylpalladium(II) hydride complex has not so far been confirmed. Presumably allylpalladium chloride interacts with the complex $HPdCl_2^-$ and is converted into $Pd_2Cl_4^{2-}$ and $CH_3CH = CHR$. In the light of new data concerning the possibility of the insertion of various molecules in the Pd–Pd bond in palladium(I) complexes, another version of the C–H bond dissociation mechanism can be suggested:



The highly reactive σ-allylpalladium chloride can interact directly with $HPdCl_2^-$ or can be first converted into a π-allyl complex as in scheme (17).

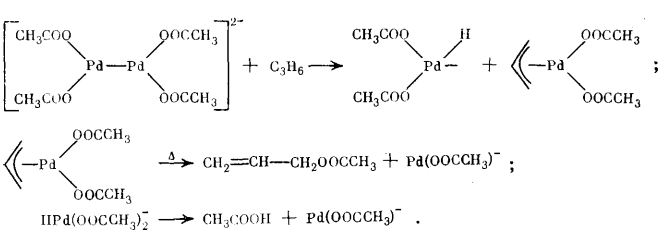
2. The Oxidation of Organic Compounds

As we have seen above, palladium(I) complexes were regarded as the final reaction products in olefin oxidation reactions. This hypothesis was confirmed chemically by Davidson and Triggs[70]. A benzenepalladium(I) complex is formed (Table 6, No.5) on reduction of palladium(II) acetate with hex-1-ene in perchloric acid-containing acetic acid in the presence of 25% of benzene. An analogous complex is formed also in the oxidative dimerisation of benzene. Under the conditions of the oxidation of cyclohexa-1,4-diene catalysed by $Pd(OOCCH_3)_2$, a palladium(I) complex was also isolated[73] (Table 6, No.7). The reduction of $PdSO_4$ by ethylene in the presence of *p*-benzoquinone (Q) results in the formation of the complex $Pd_2SO_4.Q$.[74] As mentioned above, the formation of palladium(I) in the reactions considered may be a consequence of two processes—the decomposition of intermediate organometallic σ-compounds [reaction (6)] or the reduction of palladium(II) by a zerovalent palladium complex stabilised by some kind of π ligand:

$$PdSO_4 + C_2H_4 + H_2O + Q \rightarrow Pd^0 \cdot Q + H_2SO_4 + CH_3CHO\ ;$$
$$Pd^0 \cdot Q + PdSO_4 \rightarrow Pd_2SO_4 \cdot Q\ .$$

The palladium(I) formed in the oxidative dehydrogenation of cyclohexane to benzene[71,72] exhibits an interesting "protecting" function—the benzene bound in a complex with palladium(I) is not sulphonated in 98% H_2SO_4. When oxidants capable of oxidising palladium(I) are added, only benzene sulphonation products are formed.

It is believed[130–135] that the palladium(I) complexes $[Pd_2(OOCCH_3)]_2$ (or clusters with a large number of atoms) are involved in the heterogeneous catalytic oxidative acetoxylation of olefins. The study of the XPE spectra of the catalyst $[Pd(OOCCH_3)_2 - CH_3COOK]/Al_2O_3$, prepared in different ways before and after tests for catalytic activity, showed that the specimens which have the 336.2 ± 0.1 eV band $[E(3d_{5/2})]$ in the XPE spectrum are active in the acetoxylation of propene. Politanskii et al.[135] assigned this band to the $CH_3COOPd-PdOOCCH_3$ fragment located on the catalyst surface. The specimens whose XPE spectra contain only the 335.3 or 336.8 eV bands, which the authors assigned to Pd(0) and PdO/Al_2O_3 respectively, have no catalytic activity in the process investigated[135]. A mechanism, close to the mechanism of the isomerisation of olefins, which does not specify in detail the possible modes of coordination of acetate groups, was proposed[131]:



The interaction of zerovalent palladium or of the hydride and allyl complexes with oxygen leads to the regeneration of the catalytically active form of palladium(I).

As mentioned above, the formation of paramagnetic palladium(I) centres has been established by EPR in a study of the interaction of the PdY zeolite with H_2 and CO.[9,10] Treatment of this specimen with oxygen at 500 °C with subsequent evacuation converts ~1% of palladium to the +3 state. If the same specimen is then treated with hydrogen at 25 °C, the zeolite blackens, the EPR signal corresponding to palladium(III) disappears, and the signals of two different palladium(I) states appear (8% of the total amount of palladium). The palladium(I) signals vanish when the specimen is treated with oxygen at 300 °C. The action of carbon monoxide on the specimens treated beforehand with oxygen or hydrogen leads to the disappearance of the EPR signals detected previously and to the appearance of a triplet signal, which the authors attributed to palladium(I) carbonyl[9]. Analogous results were obtained later in a different study[10]. When the zeolite specimen was treated in succession with hydrogen, carbon monoxide, and oxygen, the formation of carbon dioxide was observed. The involvement of palladium(I) carbonyl in this reaction is extremely probable[9].

Taking into account the comparatively high thermal stability of the palladium(I) complexes with isonitrile, carbonyl, and other ligands, one must bear in mind the possibility of the involvement of palladium(I) compounds as intermediates or catalysts in heterogeneous processes catalysed by palladium.

3. Oxidation of Carbon Monoxide

The oxidation of CO in solutions of palladium(I) complexes has been known since 1894 [136] and has been studied in fair detail[102,137,138]. Nevertheless, the role of the palladium(I) complexes in this reaction has started to become clear comparatively recently. It is known that CO reduces palladium(II) to palladium(I) (this is a method of synthesis of carbonyl complexes[38-41]), while $[Pd(CO)Cl]_n$ or $Pd_2(CO)_2Cl_4^{2-}$ decompose in aqueous solutions to CO_2 and zerovalent palladium[36]:

$$Pd^{II} \xrightarrow[-CO_2]{CO,\ H_2O} Pd^{I}CO \xrightarrow[-CO_2]{H_2O} Pd^0 .$$

The rate of decomposition of $[Pd(CO)Cl]_n$ increases greatly in the presence of an oxidant (Q, $Cr_2O_7^{2-}$). However, the characteristic features of the transformation of $[Pd(CO)Cl]_n$, investigated by Zhir-Lebed' and Golodov[106], left open the question of the role of palladium(I) in the CO oxidation process. Autocatalytic phenomena and a stepwise character of the reduction of palladium(II) have been observed in studies[139-141] of the reaction of $PdCl_2$ with CO without an oxidant. The inductive period was abolished after the introduction of the complex $[Pd(CO)Cl]_n$ into the initial solution ($PdBr_2$–H_2O–dioxan), and the rate of oxidation of CO increased. It follows from these findings that not only are palladium(I) complexes formed in the course of the reduction of palladium(II) but (in the absence of an oxidant) they also play the role of a catalyst of the oxidation of CO. The catalytic cycle (the chain propagation stages) in this process can be represented schematically as follows[102]:

$$[Pd_2(CO)_2X_4]^{2-} \xrightarrow{H_2O} Pd_2(COOH)(CO)X_3^{2-};$$

$$Pd_2(COOH)(CO)X_3^{2-} + PdX_2 + CO \rightarrow Pd_2(CO)_2X_4^{2-} + Pd^0 + CO_2 + HX .$$

In the presence of oxidants, the role of palladium(I) can change, but the stages involving the formation of palladium(I) complexes and their conversion into CO_2 can take place[141-143]. Studies of the kinetics of this reaction in the $PdCl_2$–$FeCl_3$–HCl–H_2O system led Brailovskii and co-workers[142,143] to the conclusion that zerovalent palladium complexes (carriers of the kinetic chain) play an important role in this system, while palladium(I) complexes are formed as a result of chain termination [Pd(0) + Pd(II)], which lowers the rate of formation of CO_2.

According to current information, there is a possibility of the direct transfer of an oxygen atom to CO from O_2 under homogeneous conditions. Thus the oxidation of CO by oxygen takes place selectively in the $Pd_4(phen)_2(CO)\cdot(OOCCH_3)_4$ cluster in acetic acid solution:[99]

$$Pd_4(phen)_2(CO)(OOCCH_3)_4 + \tfrac{1}{2}O_2 \rightarrow Pd_4(phen)_2(OOCCH_3)_4 + CO_2 .$$

4. Oxidative Carbonylation of Alcohols and Certain Other Oxidation-Reduction Reactions of Carbon Monoxide

A study of the kinetics of the catalytic carbonylation of methanol in the presence of $PdCl_2$,[102,107,144]

$$2CO + 2CH_3OH + Q \xrightarrow{PdCl_2} (COOCH_3)_2 + QH_2 , \qquad (18)$$

established that, under conditions where the rate of formation of dimethyl oxalate r_{DMO} is independent of p_{CO}, the dicarbonyl complex $PdCl_2(CO)_2$ is involved in the reaction. The rate of reaction is then described by the equation

$$r_{DMO} = \frac{k[PdCl_2(CO)_2]_\Sigma \cdot [Q]}{1 + k_1[PdCl_2(CO)_2]_\Sigma^n} ,$$

where $n = 1-2$, depending on the range of variation of $[PdCl_2]_\Sigma$. One of the hypotheses which explained the variable and fractional order of the reaction with respect to $[PdCl_2]_\Sigma$ is the possibility of the formation of palladium(I) carbonyl chloride clusters. We already noted above (Section III, subsection 3) that $[Pd(CO)Cl]_n$ is converted into the chloride carbonate in alcoholic solutions, while in the presence of p-benzoquinone it is converted into dimethyl oxalate. The carbonylation of phenol to diphenyl carbonate and salicylate also takes place in the presence of palladium(I) carbonyl halides[145,146]. However, a study[107] of the kinetics of the reaction (18) catalysed by $[Pd(CO)Cl]_n$ showed that the rate of reaction in this system under steady-state conditions (under conditions of independence of p_{CO}) is described by another equation:

$$r_{DMO} = k_2[Pd_2(CO)_2Cl_4^{2-}]_\Sigma \cdot [Q] .$$

In the region of first order of the reaction with respect to the catalyst, the constant k_2 is greater than k by a factor of 1.6. For $[Pd]_\Sigma = 0.06$ M, the rate of reaction in palladium(I) solutions is 4.5 times higher than r_{DMO} in palladium(II) solutions, other conditions being equal.

In $[Pd(CO)Cl]_n$ solutions in the presence of an excess of LiCl [when account is taken of the CO content in the initial palladium(I) carbonyl halide], one mole of CO is absorbed per gram-atom of palladium, i.e. dimeric dicarbonyl complexes, probably $Pd_2(CO)_2Cl_4^{2-}$, are formed in these solutions. Thus the results of the above investigations lead to a remarkable consequence: in a CO atmosphere in alcoholic solutions of p-benzoquinone, palladium(II) and palladium(I) form two different catalytic systems which are not interconverted to an appreciable extent. This conclusion has been confirmed in a study of the kinetics of the model reaction

$$2CH_3COOHgCOOCH_3 + Q + 2HX \rightarrow (COOCH_3)_2 + QH_2 + Hg(OOCCH_3)_2 + HgX_2$$

catalysed by $PdCl_2$ and $[Pd(CO)Cl]_n$. Different dependences of the rates of reaction on [Q] were obtained in this instance, and, for identical reactant concentrations under the conditions of first order of the reaction with respect to both Q and the catalyst, the second-order rate constant is higher by a factor of 4.2 for $PdCl_2$ than in $Pd_2(CO)_2Cl_4^{2-}$ solutions. The mechanism of the synthesis of dimethyl oxalate in palladium(I) solutions is described by the scheme[107]

$$Pd_2(CO)_2Cl_4^{2-} + Q \overset{K}{\rightleftarrows} \underset{(XVII)}{QPd_2(CO)_2Cl_3^-} + Cl^- ;$$

$$(XVII) \begin{cases} \xrightarrow[H^+,\ Cl^-]{ROH} QPd_2(COOR)(CO)Cl_2^- + Cl^- \ (XVIII) ; \\ \xrightarrow[k_2']{CH_3COOHgCOOR} (XVIII) ; \end{cases}$$

$$(XVIII) \begin{cases} \xrightarrow[H^+]{ROH} QPd_2(COOR)_2Cl_2^{2-} \ (XIX) ; \\ \xrightarrow[k_3',\ -CO]{CH_3COOHgCOOR} (XIX) ; \end{cases}$$

$$(XIX) + 2HCl \rightarrow Pd_2Cl_4^{2-} + QH_2 + (COOR)_2 ;$$

$$Pd_2Cl_4^{2-} + 2CO \rightarrow Pd_2(CO)_2Cl_4^{2-} .$$

It has been reported that the carbonyl chloride $[Pd(CO)Cl]_n$ [147] and the carbonyl acetate $[Pd(CO).(OOCCH_3)]_4$ [148] are involved in the oxidative carbonylation of olefins:

$$CH_2{=}CHR + ArOH + [Pd(CO)Cl] \xrightarrow[CH_2Cl_2;\ CO\ (1\ atm)]{R_3N;\ 20^\circ} \begin{cases} \longrightarrow ArOOCCH(OAr)CH_2R \\ \longrightarrow ArOOCCH{=}CHR \end{cases} + Pd_{met};$$

$$C_6H_5CH{=}CH_2 + CH_3OH + [Pd(CO)(OOCCH_3)]_4 \xrightarrow[28^\circ]{CO\ (1\ atm)} C_6H_5CH{=}CHCOOCH_3 + Pd_{met}.$$

The same reactions occur in catalytic systems based on palladium(II) in the presence of oxidants[102,149]. The elucidation of the role of palladium(I) compounds in the oxidative carbonylation of olefins requires further study.

The oxidative carbonylation of amines resembles closely the reactions considered in this Section[150-152]. The short inductive period in the $PdCl_2$–$CuCl_2$ system in the synthesis of dibutylurea

$$4RNH_2 + CO + CuCl_2 \xrightarrow{PdCl_2} RNHCONHR + 2CuCl + 2\overset{+}{R}NH_3Cl^-,$$

and the fractional order of the reaction with respect to $PdCl_2$ (~0.5) is treated[151,152] as a consequence of the catalysis of this reaction by palladium(I) complexes. This hypothesis cannot yet be regarded as sufficiently well founded.

Palladium complexes catalyse an interesting reaction involving the reductive carbonylation of nitro-compounds[153]:

$$RNO_2 + 3CO \rightarrow RNCO + 2CO_2.$$

It has been suggested that palladium(I) carbonyl halide complexes can participate in this reaction. Its mechanism is apparently close to that of the stoichiometric reduction of ArNO by carbon monoxide coordinated to palladium(I).[154] When equimolar amounts of ArNO and Pd(CO)Cl interact in dichlorobenzene at 90 °C, ArN–NAr and CO_2 are formed via the reaction

$$2Pd(CO)Cl + 2ArNO \rightarrow ArN{=}NAr + 2CO_2 + [Pd_2Cl_2]$$
$$[Pd_2Cl_2] \rightarrow PdCl_2 + Pd_{met}.$$

In the case of C_6H_5NO the products are ~90% of azoxybenzene and 10% of azobenzene relative to the initial C_6H_5NO.[154]

The oxidative dehydration of acetic acid is a very interesting reaction[155]:

$$2CH_3COOH + CO + \tfrac{1}{2}O_2 \xrightarrow{Pd(CH_3COO)_2} (CH_3CO)_2O + CO_2 + H_2O.$$

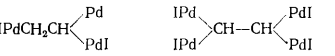
It is a coupled process. There is reason to regard palladium(I) complexes as intermediates in this reaction. It has been suggested that the reaction proceeds via the formation and transformation of the carbonyl acetate cluster [see reaction (8)]:

$$Pd(OOCCH_3)_2 \xrightarrow{CO} Pd_2(CO)_2(OOCCH_3)_2 \xrightarrow{NaOOCCH_3} (CH_3CO)_2O + CO_2 + 2Pd^0.$$

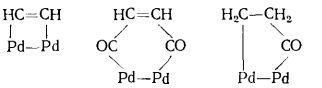
There is also a possibility of the formation of the anhydride and CO_2 in the stage leading to palladium(I). The oxidation of zerovalent palladium by oxygen or another oxidant makes the process catalytic.

5. Alkoxycarbonylation of Acetylene

The first hypothesis of the involvement of palladium(I) complexes in the oxidative alkoxycarbonylation of acetylene was put forward in a study[156] of the synthesis of maleic and fumaric diesters in the $PdCl_2$–$SC(NH_2)_2$–ROH system. The first evidence for the catalysis by palladium(I) complexes of the reactions of acetylene with RO and ROH was obtained in a study of the coupled reaction involving the synthesis of acrylic, propionic, maleic, fumaric, and succinic acid esters in the Li_2PdI_4–ROH–HCl system[51,97,102]. The potentiometric study of the active catalyst formation stage and the study of the influence of oxidants and reductants on this stage and on the rate of reaction under steady-state conditions led to the conclusion that the alkoxycarbonylation of acetylene is catalysed by palladium(I) complexes. Tests of the activities of a number of palladium(I) compounds, namely $[Pd(CO)Cl]_n$, $Cs_2Pd_2(CO)_2Cl_4$, and $Li_2Pd_2I_4.2H_2O$,[51,97] in this reaction in the LiI–C_4H_9OH system showed that palladium(I) complexes catalyse the synthesis of the acid mono- and di-esters and that the catalytic properties of $Li_2Pd_2I_4.2H_2O$ and its potentiometric characteristics are very close to the properties and characteristics of the catalytic system formed from Li_2PdI_4 after the attainment of the steady state. A study of the kinetics of this complex coupled reaction showed that the experimental dependences of the rate of formation of all the products (and their ratio) on p_{CO} and $[H^+]$ are not described by the mechanisms proposed previously[97] and not even by their combination. In order to account for the set of experimental findings, it proved essential to resort to the information about specific properties of the palladium(I) complexes and about the reactions involving the Pd–Pd bond; the products of the insertion of C_2H_2 and CO in the Pd–Pd bond (IPd–CO–CH=CH–PdI, IPd–CO–CH=CH–CO–PdI) as well as the polynuclear organometallic σ-compounds[157]



and metal-containing cyclic compounds



formed in the system were regarded as intermediates.

The study of the $PdBr_2$–$P(C_6H_5)_3$–C_4H_9OH–DMF system in the same acetylene alkoxycarbonylation reactions showed that oxidants and reductants influence the process parameters in the same way as in the Li_2PdI_4–C_4H_9OH system[158]. This influence is particularly strong in the stage involving the formation of the active complex. The hypothesis of the involvement of low-valence forms of palladium [palladium(I)] in this system does not conflict with recent data, according to which the complex $[PdClP(C_6H_5)_3]_2CO$ [$\nu(CO)$ = 1860, 1890 cm^{-1}] proved to be catalytically active in the DMF–C_4H_9OH system; the overall rate of reaction and the rates of formation of individual esters are comparable to the rates of alkoxycarbonylation in the $PdBr_2$–$P(C_6H_5)_3$–DMF–C_4H_9OH system[159].

6. The Hydrogenation, Dimerisation, and Cyclo-oligomerisation of Unsaturated Molecules

The important role of palladium(I) compounds in the mechanism of the formation of catalytically active complexes—catalysts of the hydrogenation of dienes and alkynes in the $[(C_6H_5)_3PPd(CH_3COO)_2]_2$–$H_2$ system in various solvents—has been established[50,160]. It has been shown convincingly that the interaction of the complex $[(C_6H_5)_3PPd(CH_3COO)_2]_2$ with H_2 constitutes an autocatalytic process whose mechanism has been accounted for by the formation of the zerovalent palladium complex Pd_2L_2 [$L = P(C_6H_5)_3$] catalysing the reduction of $[LPd(CH_3COO)_2]_2$ via the intermediate palladium(I) complex $Pd_2(OOCCH_3)_2L_2$, which undergoes hydrogenolysis faster than $[LPd(CH_3COO)_2]_2$ with formation of Pd_2L_2:[160]

$$[LPd(OOCCH_3)_2]_2 + H_2 \rightarrow L_2Pd_2(OOCCH_3)_3H + CH_3COOH;$$
$$L_2Pd_2(OOCCH_3)_3H \rightarrow Pd_2(CH_3COO)_2L_2 + CH_3COOH;$$
$$Pd_2(CH_3COO)_2L_2 + H_2 \rightarrow Pd_2L_2 + 2CH_3COOH.$$

On interaction with $[LPd(CH_3COO)_2]_2$, the Pd_2L_2 formed leads to $Pd_2(CH_3COO)_2L_2$:

$$Pd_2L_2 + [LPd(CH_3COO)_2]_2 \rightarrow 2Pd_2(CH_3COO)_2L_2 ;$$
$$2Pd_2(CH_3COO)_2L_2 + 2H_2 \rightarrow 2Pd_2L_2 + 4CH_3COOH .$$

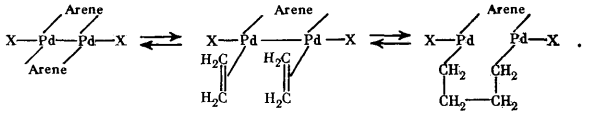
It has been established recently that the palladium cluster $Pd_5L'_2$ [$L' = P(C_6H_5)$], active in hydrogenation, is formed from Pd_2L_2 and palladium(II) [22] via the scheme

$$Pd^{II} \rightarrow Pd^{I} \rightarrow Pd_2L_2 \xrightarrow{Pd^{II}} Pd_5L'_2 .$$

Palladium clusters having the composition $\boxed{Si}\begin{matrix}P\\ \diagdown\\ \diagup\\ P\end{matrix}Pd_n$.

$.(OOCCH_3)_2$ (where n = 2, 3, 4, or 5) and immobilised on the surface have been obtained by the reaction of $Pd(CH_3COO)_2$ with zerovalent palladium on a silica gel surface modified by the diphosphine ligand $\boxed{Si}-P_2$ and also from the complex $[Pd_2(CO)_2(OOCCH_3)_2]_2$ and $\boxed{Si}P_2$.[64] The complex with n = 2 [formally of palladium(I)] resembles closely palladium(I) complexes according to XPE spectroscopy and is converted by triphenylphosphine into the complex $Pd_2(OOCCH_3)_2L_2$ described by Berenblyum et al.[50¶] The immobilised complex with n = 2 catalyses the hydrogenation of cyclopentadiene; the ratio of the rates of hydrogenation of cyclopentadiene and cyclopentene is in the range 0.2–1.[161]

The first information about the catalytic dimerisation of ethylene in solutions of palladium(I) complexes has appeared recently[69]. The aromatic π-complexes $(ArH)_2Pd_2(Al_2Cl_7)_2$ and $(ArH)_2Pd_2(AlCl_4)_2$ in benzene and toluene (ArH = benzene, toluene, or p-xylene) form a mixture of *trans*-but-2-ene (80%) and *cis*-but-2-ene (14–20%) at room temperature at a rate greatly exceeding the rate of dimerisation in palladium(II) solutions (~25 moles of butene per hour per gram-atom of palladium). The catalytic system is stable only in aromatic solvents. A mechanism incorporating a stage involving the oxidative addition of two ethylene molecules to the Pd-Pd bond has been proposed:

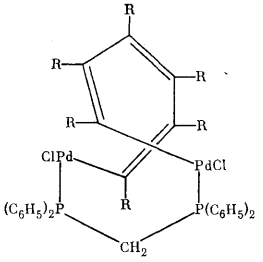


(XX) (XXI) (XXII)

According to Pertici and Vitulli[69], the reaction of compound (XXII) takes place synchronously because palladium atoms promote the transfer of two hydrogen atoms with formation of the primary product—*trans*-but-2-ene.

The possible involvement of palladium(I) complexes also in the polymerisation of propene to polyethylene, catalysed by palladium(II) cyanide, has been suggested[104]. The transfer of hydrogen from one propene molecule to another can take place via a mechanism similar to that of the isomerisation of butene [reaction (17)] on the fragment containing NCPd–PdCN. The available information about the existence of the complex $Pd_2(CN)_6^{4-}$ even in aqueous solutions (see Section III, subsection 3) makes this hypothesis entirely probable.

In connection with the synthesis of the products of the insertion of acetylenes and olefins in a Pd–Pd bond[122], the activity of the complex $Pd_2(dpm)_2Cl_2$ in the cyclotrimerisation of dimethyl acetylenedicarboxylate was tested. The complex proved to the active, like the complex $Pd_2(dpm)_2$. $.[\mu\text{-}C_2(COOR)_2]Cl_2$, formed under reaction conditions and capable of being an intermediate in the synthesis of hexamethyl mellitate. The reaction takes place at room temperature with formation of 10–13 moles of the product per hour per mole of the complex. The subsequent insertion of three alkyne molecules in the Pd–Pd and Pd–C bonds can lead to the intermediate (XXIII) in which the Pd atoms linked to the bisphosphine ligand are in a position convenient for the reductive elimination reaction with ring closure [like the complex $(RC_2R')_3Co_2(CO)_4$] [163] and the formation of benzene derivatives.



(XXIII)

In conclusion of this Section, we may note that, for the understanding of the mechanisms of a large number of catalytic processes, it is useful to resort to the hypothesis of the involvement of the Pd–Pd cluster bond of palladium(I) complexes in the formation of intermediates compounds in catalytic reactions. The presence of the Pd–Pd fragment in the catalytically active complexes may promote the formation of metal-containing rings with a metal–metal bond and can lead to partial reduction of a number of substrates (CO, RNC, C_2R_2) as a result of their oxidative addition to Pd_2, to the formation of Pd–C bonds as a consequence of the rupture of the Pd–Pd bonds, and to the homolytic rupture of C–H bonds at two centres. Judging from all the considerations, palladium(I) complexes are in general convenient models for the study of catalysis by metal clusters.

* * *

Thus compounds of palladium in the +1 oxidation state constitute a fairly numerous family with a number of structural features associated with the presence of a metal–metal bond. The possibility of the extensive variation of the oxidation-reduction properties of palladium(I) by varying the nature of the ligands is extremely important for catalysis by palladium(I) complexes because the range of variation of the standard electrode potential of the Pd(II)/Pd(I) pair is very large, amounting to ~2.7 V.

The data presented above show that palladium(I) compounds can exist in aqueous, non-aqueous, and non-polar media under different conditions, including high temperatures and in the presence of oxidants (oxygen, *p*-benzoquinone). The appearance of palladium(I) compounds under the conditions of catalytic processes can lead to the operation of unusual mechanisms due to the presence of the Pd–Pd bond.

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The Mechanism of the Oxidative Coupling of Unsaturated Hydrocarbons Under the Influence of Palladium(II) Complexes

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The results of studies on the mechanism of liquid-phase reactions involving the oxidative coupling of arenes to biaryls, of arenes and olefins to arylolefins, and of olefins to 1,3-dienes under the influence of palladium(II) complexes are surveyed. The bibliography includes 161 references.

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I. INTRODUCTION

The liquid-phase reactions involving the oxidative coupling of unsaturated hydrocarbon to biaryls, arylolefins, and 1,3-dienes under the influence of palladium(II) complexes have been discovered and widely investigated in the course of the last twenty years[1-3]. In a general form, they can be represented by the equation

$$RH + R'H + Pd^{II} \rightarrow R{-}R' + Pd^{0} + 2H^{+}, \quad (1)$$

where R, R′ = aryl or alkenyl. These reactions involve the formation of a new C–C bond and as a rule give rise to products with a conjugated system of π-bonds. The oxidative coupling of hydrocarbons has come to be widely used synthetically because of its many advantages over traditional methods. These include simplicity, universality, and the possibility of carrying out catalytic reactions by oxidising zerovalent palladium to palladium(II) *in situ*. The importance of these reactions is indicated by the abundance of publications devoted to them[4-18].

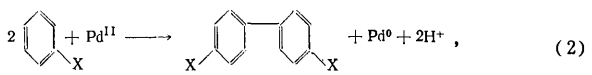
Qualitative hypotheses concerning the mechanism of the oxidative coupling of hydrocarbons and based on the fundamental reactions of organometallic chemistry were put forward a long time ago[4-18]. The formation of a new C–C bond is treated as a result of a sequence of π–σ transformations of the substrate in the coordination sphere of palladium(II). Here the key stage is the formation of the reactive intermediate RPdX with a C–Pd σ-bond. The hypothesis of the π–σ rearrangements proved useful in metal complex catalysis[19]. However, it does not provide a detailed picture of the reaction mechanism. The questions of the rate-limiting stage, the active form of palladium(II) compounds, the role of π-complexes of RH with palladium(II), and others remain obscure. An answer to these questions has been obtained only recently as a result of detailed kinetic studies of reaction (1) and also the synthesis of organopalladium compounds and the study of their reactions.

The aim of the present review is to survey the results of studies on the mechanism of the oxidative coupling of unsaturated hydrocarbons under the influence of palladium(II) complexes.

II. THE COUPLING OF ARENES

1. General Considerations

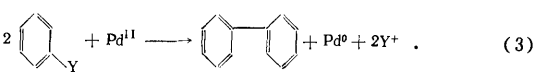
The coupling of arenes takes place under the influence of palladium(II) salts in organic and more rarely aqueous solutions at a temperature which does not usually exceed 120 °C:[1,16,20,21]



(2)

where X = H, alkyl, halogen, aryl, OR, CO_2R, OCOR,[1] NO_2,[22] OH,[23] etc. In the general case a mixture of all the theoretically possible biaryl isomers is formed (six isomers for PhX), their proportions being determined by the nature of the substituents in ArH.[1,21,24]

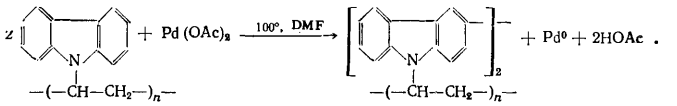
The coupling of organoelemental compounds takes place much more readily and selectively:



(3)

These include the aryl derivatives of mercury(II),[25-27] magnesium(II),[28] thallium(III),[29,30] tin(IV), lead(IV),[25] and boric[21] and sulphinic[31] acids. The mercury(II) compounds are most frequently used.

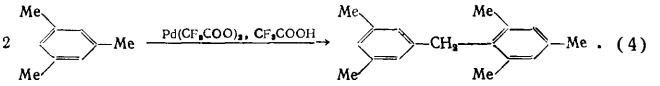
The coupling of arenes takes place in a large series of aromatic systems[16]. Derivatives of benzene[23-32] and napthalene[33,34], heterocyclic compounds[14,35-42], metallocenes[43,44], etc. undergo this reaction. The aromatic groups of polymers undergo intermolecular coupling[42]:



In the presence of oxidants capable of oxidising zerovalent palladium to palladium(II), catalytic coupling takes place[16]. Copper(II),[25,33,37-39] thallium(III),[29,30] and iron(III)[39,45]

salts, V_2O_5,[39] vanadium(V)-containing heteropolyacids[41,46,47], nitrogen oxides[48], and molecular oxygen[34,49-54] have been used as oxidants in homogeneous systems. Heterogeneous catalysts of the coupling of arenes are also known[16,55]. The yields of biaryls in the catalytic process reach hundreds of moles per mole of palladium(II).[52]

The pathway followed in the reactions of arenes depends on the nature of the ligands in the palladium(II) complexes. Inorganic acids, for example, $HClO_4$, catalyse the coupling of arenes[20,21,26,56]. The reaction of benzene and $Pd(ClO_4)_2$ in acetic acid takes place with a quantative yield of biphenyl[56]. In the presence of $Pd(OAc)_2$ in acetic acid, ArH undergoes acetoxylation in the ring and in the side chain as a side reaction[20,21,50,57-59]. In the presence of $Pd(CF_3COO)_2$, the contribution of these reactions is smaller[60]. Acetate ions promote the acetoxylation[20,57], while inorganic acids and oxygen suppress it[20,21,50]. The ring acetoxylation of ArH has been widely investigated as a potential method of synthesis of phenols[36,51,61-64]. There is reason to believe that the acetoxylation of methylbenzenes in the side chain is catalysed by palladium clusters[65,66]. When $Pd(NO_3)_2$ is used, the coupling is accompanied by the nitration of arenes[48,67,68]. In acid media the reaction of palladium(II) with methylbenzenes gives rise to diarylmethanes together with biaryls[21,22]:



. (4)

Among promising reactions mention may be made of the coupling of polymethylbenzenes as a method of synthesis of biphenylpolycarboxylic acids, which are valuable monomers for polycondensation[18]. The coupling of phthalic acid esters is of interest from this standpoint. The coupling of furan derivatives can be used to synthesise long-chain α,ω-bifunctional compounds, for example, dicarboxylic acids. Thus, in the presence of $Pd(OAc)_2$ and $CuCl_2$, furfural and pyromucic acid esters are smoothly converted into 2,2'-bifuryl derivatives[38], from which sebacic acid can be obtained by the cleavage of the furan ring[69].

2. The Mechanism of the Coupling of Arenes

(a) *Palladium(II) acetate complexes.* Reaction (1) proceeds with different palladium(II) compounds, but preference is usually given to palladium(II) acetate. The latter is trimeric in the crystalline state[70]. In benzene at 37 °C and in acetic acid at 25 °C it is also trimerised, but depolymerises on heating[70-73]. At 80 °C in benzene, palladium(II) acetate is monomeric[70].

Palladium(II) salts of strong acids show a smaller tendency towards association. Thus $Pd(CF_3COO)_2$ is monomeric in benzene at 37° and 80 °C.[70]

On heating in acetic acid solution, the $Pd_3(OAc)_6$ trimer slowly dissociates to the monomer:

$$Pd_3(OAc)_6 \overset{K_{3,1}}{\rightleftarrows} 3Pd(OAc)_2 .$$

$K_{3,1} = 2.7 \times 10^{-10}$ mol^2 litre^{-2} at 75 °C.[71] In the presence of sodium or lithium acetate, palladium(II) acetate depolymerises even at 25 °C and the following equilibria are established:

$$2Pd_3(OAc)_6 + 6NaOAc \overset{K_{3,2}}{\rightleftarrows} 3Na_2Pd_2(OAc)_6 , \quad (5)$$

$$Na_2Pd_2(OAc)_6 + 2NaOAc \overset{K_{2,1}}{\rightleftarrows} 2Na_2Pd(OAc)_4 , \quad (6)$$

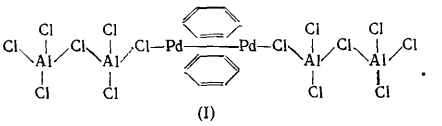
where $K_{3,2} = 7.77 \times 10^4$ litre^5 mol^{-5} and $K_{2,1} = 7.6 \times 10^{-4}$ litre mol^{-1} at 25 °C in acetic acid. In the presence of 0.2 M sodium acetate, the trimer is fully converted into the dimer $Na_2Pd_2(OAc)_6$.[72]

Palladium(II) acetate polymers readily decompose on treatment with ligands L such as pyridine, bipyridyl, Me_2SO, PPh_3, and $AsPh_3$ with formation of the complexes *trans*-$Pd(OAc)_2L_2$,[70] which undergo the *cis–trans* isomerisation in solution[74,75]. The slow interaction of $Na_2Pd_2(OAc)_6$ with olefins takes place similarly[76].

Palladium(II) acetate and chloride complexes have similar stability constants in aqueous solution[77] and for this reason palladium(II) chloride is converted into the acetate in the presence of an excess of sodium acetate.

The palladium(II) acetate monomer, dimer, trimer can have different reactivities[78,79]. If reactions (5) and (6) are used for their synthesis, then account must be taken of the possibility of base catalysis by the acetate ion in the determination of the relative reactivities of these species.

(b) *Arenes as ligands.* There is sufficient reason to assume that π-arene complexes of palladium(II) are intermediates in the oxidative coupling of arenes. π-Arene complexes are known for many metals, including palladium[80]. The diamagnetic complex $[Pd(C_6H_6)Al_2Cl_7]_2$, containing palladium in the formal +1 oxidation state, has been obtained by the Friedel–Crafts reduction. The complex has the structure



(I)

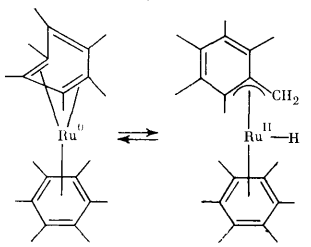
The lengths of the Pd–Pd and Pd–Cl bonds are 2.58 and 2.46 Å respectively and the Cl–Pd–Pd–Cl atoms are located virtually on a straight line[81].

When benzene was coupled under the influence of palladium(II) acetate in acetic acid in the presence of 0.5 M $HClO_4$ at 50 °C, the palladium(I) complex $[Pd(C_6H_6)(H_2O)ClO_4]_n$ where apparently $n = 2$ (Rudakov et al.[82]), was isolated[21], but its role in the reaction was not established. An analogous complex has been detected by NMR in the interaction of benzene with $PdSO_4$ in 90% sulphuric acid[82]. The complex Pd_2SO_4.(quinone).$3H_2O$ was isolated[83] in the oxidation of olefins to carbonyl compounds in an acid aqueous solution in the presence of quinone and $PdSO_4$. Virtually all the known palladium(I) complexes are diamagnetic and contain an even number of palladium atoms[84].

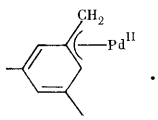
The less stable arene complexes of palladium(II) have not been isolated, but their formation in reaction (1) has been detected by kinetic methods. The coupling of thiophen to bithienyl under the influence of $Pd_3(OAc)_6$ in acetic acid obeys the Michaelis equation; the stability constant of the thiophen complex of palladium(II) $K = 0.2$ litre mol^{-1} at 70 °C.[40] The arylation of styrene on treatment with $Pd_3(OAc)_6$ in acetic acid at 70 °C was similarly found to have $K = 0.11$ and 4.6 litre mol^{-1} for benzene and naphthalene; in both cases ΔH is close to zero[85]. In the oxidative coupling of benzene in 90% sulphuric acid under the influence of $PdSO_4$, the π-complex $(C_6H_6)Pd(II)$ with $K = 17$ litre mol^{-1} at 23 °C was detected by NMR.[82]

Both all the π-electrons of ArH and only some of them can participate in the formation of the bond between the metal ion and the arene[18]. Thus, in the complex $(Me_6C_6)_2Ru(0)$ one ring is involved in complex formation symmetrically (η^6), while the other is involved with participation of two double

bond (η^4) and the free C–C bond is located to one side of Ru(0) and has the usual length of 1.33 Å.[86] It is assumed that in solution there is equilibrium with the π-benzyl hydrido-complex of ruthenium(II):[87]



It has been suggested[22] that the formation of diarylmethanes in the oxidative coupling of methylbenzenes [reaction (4)] proceeds via π-benzyl complexes:



(c) *Stoichiometric mechanism.* It is generally accepted that the oxidative coupling of arenes proceeds via electrophilic substitution as the rate-limiting stage[4,5,10,11,16,88,89],

$$ArH + PdX_2 \rightleftarrows \pi\text{-}ArH \cdot PdX_2 \rightarrow ArPdX + HX\,, \qquad (7)$$

which constitutes a π–σ reaction of ArH in the coordination sphere of palladium(II). The coupling of arenes is in fact accelerated by electron-donating and retarded by electron-accepting substituents in ArH; the isomeric composition of the biaryls is characteristic of electrophilic substitution reactions, at any rate for coupling in acid media[1,21,22,24,47]. The reaction proceeds in accordance with the kinetic equation[1,21,40,56]

$$W = k[Pd^{II}][ArH]\,, \qquad (8)$$

is catalysed by bases[40], and exhibits a powerful isotope effect: $k_H/k_D = 5.0$.[21,24] Certain azo-coupling reactions, which are typical examples of electrophilic aromatic substitution, possess analogous properties[90]:

$$ArN_2^+ + Ar'H \rightarrow ArN{=}NAr' + H^+\,.$$

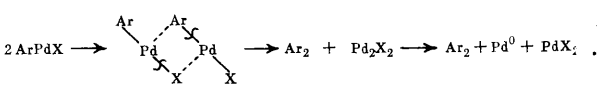
Reaction (7) is confirmed also by the finding that the coupling of arenes proceeds much more readily when one uses aromatic organoelemental compounds in which the element can be substituted by palladium(II), for example ArHgX (Eqn.(3)).[26]

Several pathways have been suggested for subsequent rapid reactions of ArPdX.[1,10,14,16,21,22,89,91] The mechanism involving the symmetrisation of ArPdX with formation of Ar_2Pd and subsequent reductive elimination of biaryl from Ar_2Pd is best supported by evidence[16]:

$$2ArPdX \rightarrow Ar_2Pd + PdX_2\,, \qquad (9)$$

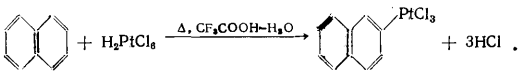
$$Ar_2Pd \rightarrow Ar_2 + Pd^0\,. \qquad (10)$$

One cannot rule out the synchronous formation of biaryl in a dinuclear complex:



The possibility of reactions (9) and (10) has been demonstrated by the occurrence of similar reactions when aryl and alkyl derivatives of palladium(II), stabilised by phosphine ligands, are used[92–95].

Aryl derivatives of platinum(IV) without phosphine ligands and functioning as intermediates in the oxidative coupling of arene under the influence of platinum(IV) have been obtained recently[96]:



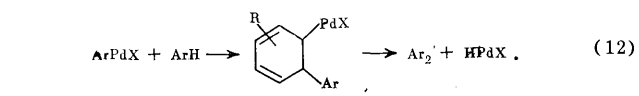
The structure of β-naphthylplatinum(IV) has been determined.

Repeated electrophilic substitution, which proceeds via an aryl-arene complex with palladium(II), has been considered as another pathway leading to the formation of biaryls[13,18,26,54]:

$$ArPdX + ArH \rightarrow [ArPd \cdot ArH] \rightarrow Ar_2 + Pd^0 + H^+\,. \qquad (11)$$

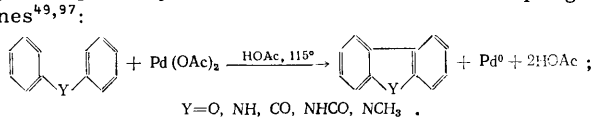
Stage (11) is possible in individual instances, for example, in the coupling of organoelemental compounds, but it is not apparently a stage in the general mechanism of the coupling of arene[16].

It is believed[22] that the coupling of arenes can proceed via the arylpalladisation of ArH and the β-elimination of palladium hydride:



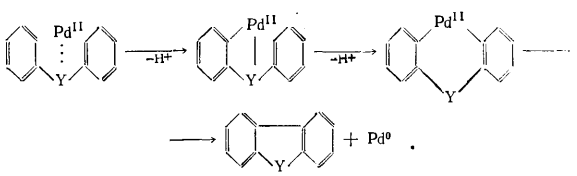
The choice between stage (9), on the one hand, and stages (11) and (12) on the other, can be made on the basis of the relative rates k/k_0 (relative to benzene) and the isotope effects k_H/k_D in the coupling of arenes[24]. It has been found that the values of k/k_0 for the coupling of toluene, measured in separate and competing reactions of benzene and toluene, agree. The isotope effects in the rates and products of the coupling of C_6H_6 and C_6D_6 have also proved to be equal. This confirms the mechanism involving stages (7), (9), and (10) but disagrees with the involvement of stages (11) and (12), because in the separate reactions the ratios k/k_0 and k_H/k_D depend on the rate-limiting stage (7), while in the competing reactions they depend on all the stages in which ArH participates and the dissociation of a C–H bond takes place.

Stage (11) probably occurs in the intramolecular coupling of arenes[49,97]:



Y=O, NH, CO, NHCO, NCH_3 .

The reaction takes place with a high yield of 2,2′-coupling products (60–90%) and apparently involves the *ortho*-palladisation of the arene by a palladium(II) complex with an *n*-donor group Y. The structure of ArPdX is favourable for the repeated intramolecular electrophilic substitution:



The *ortho*-metallation of aryl derivatives of nitrogen and phosphorus by Group VIII metal salts and complexes is well known[98].

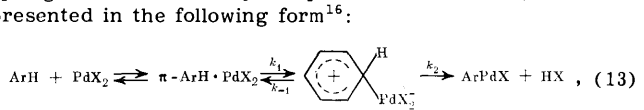
In the coupling of arenes the formation of free radicals is ruled out because phenol has not been found in the products of the coupling of benzene in an atmosphere of O_2,[1] the inhibitors of free radicals have no effect[49], and there is no H–D exchange between the arene and the solvent[21].

The detection of palladium(I) compounds in the coupling products[21] raises the question of the possible involvement of the reduced forms of palladium as intermediates in this reaction[21,82,99]. Many instances of catalysis by palladium(I) complexes and palladium clusters of liquid-phase oxidation reactions have been discovered recently[65,66,100–104]. In such reactions the initial compounds may be palladium(II) derivatives. The active reduced forms of palladium are formed in the course of the reaction, which leads in certain instances to the appearance of an inductive period[100,101]. In contrast to palladium(II) compounds, palladium clusters do not usually play the role of stoichiometric oxidants but act as catalysts in the presence of O_2.[100,104]

The question of the role of palladium(I) in oxidative coupling reactions has been investigated inadequately. However, a number of data show that palladium(I) compounds have only an indirect bearing on such reactions, at least under the most typical conditions—in aqueous acetic acid media. Indeed, the coupling of arenes can proceed both stoichiometrically and catalytically—in the presence of oxidants capable of oxidising the reduced forms of palladium [Pd(0), Pd(I), and Pd(II)].[37–39,47]. The stoichiometric reaction takes place without an inductive period, obeying the kinetic equation (8) up to the complete conversion of palladium(II),[1,40] which shows that palladium(II) is responsible for the coupling of arenes. Palladium(I) compounds are probably formed in a side reaction of zerovalent palladium with palladium(II) and are stabilised as a result of the coordination of the arene. This applies equally to other oxidative coupling reactions of unsaturated hydrocarbons considered here.

The mechanism of reactions (7), (9), and (10) is examined in detail below.

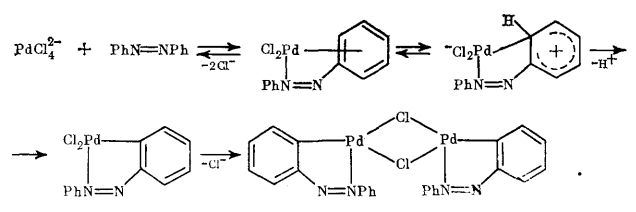
(d) *Palladisation of arenes.* The rate-limiting stage in the coupling of arenes, namely the palladisation of ArH, can be represented in the following form[16]:



(13)

where the cyclohexadienylpalladium(II) derivative is the usual intermediate in electrophilic aromatic substitution[90]. The palladisation of ArH is probably a common stage in many oxidation reactions of arenes catalysed by palladium(II), such as the arylation of olefins, the acetoxylation and nitration of ArH, etc. The mechanism of reaction (13) is therefore of considerable interest.

Direct data on reaction (13) have been obtained for the *ortho*-palladisation of azobenzenes, which leads to the formation of stable cyclic metal-containing compounds. The following mechanism has been proposed for this reaction[98]:



Metallation in the *ortho*-position has been confirmed by X-ray diffraction, the synthesis of deutero-derivatives of arenes in the reduction of palladisation products by $LiAlD_4$, and the analysis of the products of the insertion of CO in the Ar–Pd bond[98]. That *ortho*-palladisation is a kind of electrophilic substitution is indicated by the influence of the substituents in the aromatic ring on the rate of reaction[98].

ortho-Palladisation is catalysed by bases (amines, carboxylate ions, and OH^-), which facilitate the elimination of a proton[98,105]. The dependence of the rate of this reaction on the concentration of the base B is of the type $W = a[B]/\{[B] + c\}$, where a and c are constants[105]. Certain azo-coupling reactions are characterised by a similar relation[90].

The majority of data on the mechanism of the palladisation of arenes, which are discussed below, have been obtained indirectly in the study of the oxidative coupling of arenes[24,88]. In stages (9) and (10) the initial location of palladium(II) in the aromatic ring is retained, which is confirmed by numerous data concerning reaction (3). Thus in the coupling of both 4-tolylmercuroacetate and 4,4′-ditolylmercury(II) under the influence of palladium(II) and under conditions which rule out the isomerisation of the substrate, only 4,4′-bitolyl is formed[26]. Thus the rate of coupling of arenes and the isomeric composition of the biaryls correspond unambiguously to the rate and selectivity of reaction (13).[24,88]

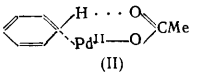
The palladisation of ArH proceeds in conformity with the kinetic equation (8) and is catalysed by strong acids ($HClO_4$)[21,26,56,88] and bases[40]. Eqn.(8) holds for both monomeric palladium(II) complexes[1,21,56] and under the conditions corresponding to the existence of palladium acetate dimers and trimers[40].

Reaction (13) with palladium(II) acetate in acetic acid has a strong primary isotope effect $k_H/k_D = 5.0$ (at 50 °C),[21] which does not change when the concentration of perchloric acid in the reaction mixture is varied from 0 to 0.86 M.[24] It has been noted that there is no isotope exchange between ArH and the solvent[21,106]. Hence it follows that the rate of palladisation of arenes is limited by the irreversible stage (k_2) involving the elimination of a proton from the cyclohexadienyl intermediate; the stage governed by the constants k_1 and k_{-1} involved rapid equilibration. It is noteworthy that mercuration of benzene by mercury acetate in acetic acid is to some extent limited by the stage with k_1 and k_{-1}. This is indicated by the increase of k_H/k_D from 3.2 to 6.0 with increase of perchloric acid concentration from 0 to 0.32 M.[107]

The catalysis by $HClO_4$ can be explained by the increase of k_1 as a result of the formation of more reactive palladium(II) perchlorate complexes[26] and also by the increase of k_2 as a consequence of the increase of the inductive effect of palladium(II) in the cyclohexadienyl intermediate on substitution of $X = OAc^-$ by ClO_4^-.

In the reaction of benzene with palladium(II) acetate in 94% acetic acid at 50 °C, the solvent was found to have the isotope effect $k_{DOAc}/k_{HOAc} = 2.7$; in the presence of 0.43 M perchloric acid, it is smaller (1.3).[24] These data apparently show that, in aqueous acetic acid in the absence of perchloric acid, the active form of palladium(II) acetate is the monomer PdOAc(OH), formed on dissociation of the trimer: $Pd_3(OAc)_6 + H_2O \rightleftharpoons PdOAc(OH) + Pd_2(OAc)_4 + HOAc$. Since the acid DOAc in D_2O is weaker than HOAc in H_2O ($K_H/K_D = 3.2$ at 25 °C [108]), the dissociation equilibrium of $Pd_3(OAc)_6$ in DOAc–D_2O is more displaced to the right compared with the equilibrium in HOAc–H_2O. In the presence of perchloric acid, palladium(II) exists predominantly in the form of monomeric perchlorate complexes and for this reason a weak isotope effect is observed.

It has been suggested that the palladisation of arenes proceeds in a single stage via the transition state



(II)

in which there is simultaneous formation of the C–Pd bond and proton transfer to the acetate ligand[56]. However, in reality there is no grounds for ruling out the generally accepted two-stage electrophilic substitution mechanism involving a cyclohexadienyl intermediate[90].

The possibility of proton transfer to the ligand in the cyclohexadienyl intermediate had been suggested previously in the mercuration of arenes[107,109]. This mechanism probably operates in the palladisation of arenes in weakly basic media, for example, in the arylation of arenes in benzene. In aqueous and aqueous organic solutions in the presence of strong inorganic acids, the solvent is more likely to be the proton acceptor, because its basicity is higher than that of the ligand. The linear dependence of the rate of coupling of benzene under the influence of $Pd(ClO_4)_2$ in 70% acetic acid on the perchlorate acid concentration is consistent with this postulate[56]. When a proton is transferred to the ligand, a linear dependence of the rate of coupling on the Hammett function h_0 would be expected[110].

Table 1 presents data on the site of substitution, the relative rates k/k_0, and the partial rate factors f_o, f_m, and f_p for the palladisation of arenes in acetic acid. They were obtained by analysing the products of the competitive coupling of arenes[24]. In acid media, in the presence of $HClO_4$ or other strong acids, the site of substitution is characteristic of electrophilic substitution, although the positional selectivity (the selectivity of attack on different positions in the ring) is much lower than for other reactions of this class[24,88]. The Hammett equation $\lg f_p = \rho\sigma^+$ holds (Fig. 1).[24] The values $\rho = -0.7 - -2.2$ [24,88] are significantly higher than for typical electrophilic aromatic substitution reactions: $\rho = -5 - -11$, [111] i.e. palladisation has a low substrate selectivity.

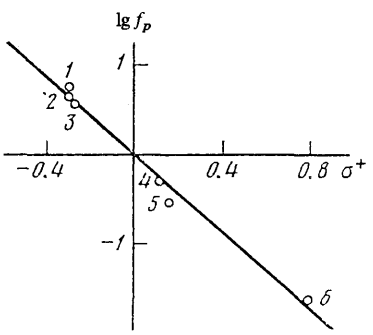


Figure 1. Dependence of $\lg f_p$ on σ^+ for the palladisation of arenes by palladium(II) acetate in acetic acid in the presence of 0.25 M $HClO_4$ at 20 °C; $\rho = -2.22$: *1*) PhMe; *2*) PhEt; *3*) iso-PrPh; *4*) PhCl; *5*) PhBr; *6*) $PhNO_2$.[24]

The selectivity in palladisation decreases with decrease of perchloric acid concentration, although its mechanism does not change under these conditions, since k_H/k_D is independent of the perchloric acid concentration[24]. An unexpected result was obtained for the reaction of toluene with palladium acetate in the absence of added strong acids: the relative contents of the *o*-, *m*-, and *p*-isomers are 5.8, 62, and 32%, i.e. the usual mode of electrophilic substitution is reversed. The yields of the *m*- and *p*-isomers are nearly statistical[24,88]. This anomaly is discussed below (see also Refs. 1, 14, and 22).

The palladisation in the *ortho*-position in a monosubstituted arene is controlled to a greater extent by the steric influence of the substituent than by its electronic influence. This can be seen from the decrease of f_o in the sequence PhMe > PhEt > iso-PrPh (Table 1). The bulk of the attacking species is also important in the *ortho*-attack. Thus in the palladisation of toluene in acetic acid, the yield of *o*- and *p*-isomers decreases with decrease of the perchloric acid concentration from 0.86 M to zero. However, f_p decreases only by a factor of 3, while f_o decreases by a factor of 8. The state of palladium(II) in solution changes under these conditions: the monomer $Pd(ClO_4)_2$ is converted into the trimer $Pd_3(OAc)_6$. The latter is evidently subjected to a stronger steric hindrance in attack on the *ortho*-position of toluene[24].

Table 1. The mode of substitution and the partial rate factors *f* for the palladisation of arenes in acetic acid {[ArH] = 2.5 M, $[Pd(OAc)_2]$ = 0.050 M, $[H_2O]$ = 0.95 M, 20 °C}.[24]

ArH	$[HClO_4]$	Content of isomers, %			k/k_0^*	f_o	f_m	f_p
		ortho	*meta*	*para*				
PhMe **	—	5.8	62	32	0.90	0.16	1.7	1.7
PhMe **	0.017	7.6	49	43	1.08	0.25	1.6	2.8
PhMe **	0.086	15	39	46	1.44	0.65	1.7	4.0
PhMe **	0.43	19	32	49	1.74	1.0	1.7	5.1
PhMe **	0.86	23	30	47	1.76	1.2	1.6	5.0
PhMe	0.25	23	29	48	1.93	1.3	1.7	5.5
PhEt	0.25	12	38	50	1.44	0.52	1.6	4.4
iso-PrPh	0.25	3.8	45	51	1.21	0.14	1.6	3.7
PhCl	0.25	27	29	44	0.18	0.14	0.16	0.46
PhBr	0.25	34	31	35	0.13	0.13	0.16	0.28
$PhNO_2$	0.25	0	71	29	0.013	0	0.028	0.023

*k_0 corresponds to the reaction of benzene.
**At 50 °C and for [ArH] = 1.5 M and $[H_2O]$ = 3.4 M.

The increase of f_p in the sequence iso-PrPh < EtPh < MePh is remarkable, illustrating the influence of hyperconjugation in the palladisation of arenes[24].

The palladisation reaction is compared in Fig. 2 with other aromatic substitution reactions in relation to the reactions of toluene in terms of the Brown selectivity ratios $\lg f_p = a \lg (f_p/f_m)$ (for toluene, $a = 1.31$).[111] The selectivity ratio characterises the relation between the substrate selectivity f_p and the positional selectivity f_p/f_m of the substitution in the ring of ArH. Evidently, palladisation is the least selective reaction in the series of electrophilic aromatic substitution processes, its selectivity approaching that of radical substitution, which is nearly statistical with respect to *m*- and *p*-isomers.[88]

The low selectivity in the palladisation of arenes indicates the compensation of the polar (electronic) effects of the substituents in the ArH ring[88]. Such compensation is possible as a result of the $d\pi$–$p\pi$ binding in the π-arene complex of palladium(II). The π-ArH.PdX_2 linkage is achieved as a result of the transfer of electron density from the occupied $p\pi$ orbitals of arene to the unoccupied *s*, *p*, and *d* orbitals of palladium(II) and in the reverse direction from the occupied *d* orbitals of palladium(II) to the vacant antibonding π orbital of ArH (dative bond). The operation of two mechanisms of the transfer of electron density creates conditions for the compensation of the polar influence of the substituent on the reaction centre[88]. With increase of the

"rigidity" of the ligand environment of palladium(II), for example, following the introduction of the electron-accepting ligand ClO_4^-, the efficiency of the compensation diminishes as a consequence of the weakening of the dative bond. Both the selectivity of the palladisation and its rate then increase. These qualitative ideas make it possible to explain the anomalous mode of substitution in the palladisation of arenes. However, they require a more rigorous quantum-chemical justification.

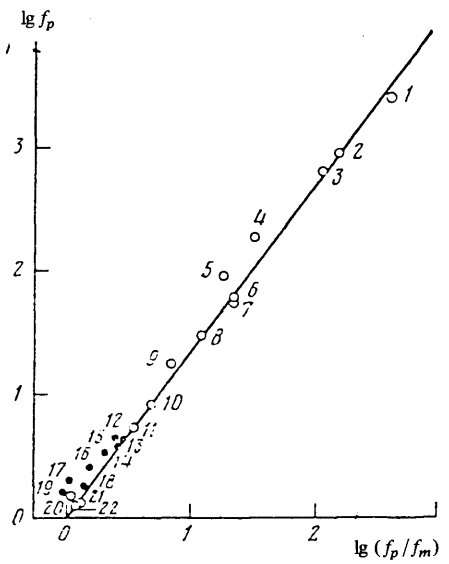


Figure 2. The ratio of selectivities for substitution in the toluene ring[88]; filled circles—reactions with palladium(II): *1*) bromination (Br_2 in 85% acetic acid, 25 °C);[111] *2*) chlorination (Cl_2 in acetic acid, 25 °C);[111] *3*) benzoylation (PhCOCl in nitrobenzene, 25 °C);[111] *4*) thallation [$Tl(CF_3COO)_3$ in trifluoroacetic acid, 10 °C];[112] *5*) ditto, 73 °C;[112] *6*) nitration (HNO_3 in 90% acetic acid, 45 °C);[111] *7*) thallation [$Tl(OAc)_3$ + H_2SO_4 in acetic acid, 70 °C];[114] *8*) mercuration [$Hg(OAc)_2$ + $HClO_4$ in acetic acid, 50 °C];[111] *9*) ditto [$Hg(OAc)_2$ in acetic acid, 50 °C];[111] *10*) sulphonation ($MeSO_2Cl$ + $AlCl_3$, 100 °C);[111] *11*) iso-propylation (iso-PrBr + Ga_2Br_6, 25 °C);[111] *12*) palladisation [$Pd(OAc)_2$ + H_2SO_4 in acetic acid, 95 °C];[88] *13*) ditto [$Pd(OAc)_2$ + $HClO_4$ in acetic acid, 55 °C];[88] *14*) ditto, 95 °C;[88] *15*) ditto ($PdCl_2$ + NaOAc in acetic acid, 90 °C;[88] *16*) ditto [$Pd(OAc)_2$ + CF_3COOH in acetic acid, 95 °C];[88] *17*) ditto [$Pd(OAc)_2$ + NaOAc in acetic acid, 95 °C];[88] *18*) catalytic coupling [$Pd(OAc)_2$ in ArH, 25 atm O_2, 150 °C];[53] *19*) palladisation [$Pd(OAc)_2$ in acetic acid, 95 °C];[88] *20*) radical arylation (attacking radical *p*-$NO_2C_6H_4$, 20 °C);[113] *21*) ditto (*p*-$MeC_6H_4^{\cdot}$);[113] *22*) ditto ($Ph^{\cdot}$).[113]

It is of interest to compare the palladisation of arenes with their mercuration. It is generally accepted that the mercuration of ArH, at least in polar media, is a type of electrophilic substitution[90]. The palladisation and mercuration of arenes are characterised by a profound similarity of the mechanisms, which is confirmed by the clear-cut correlation between their rates (Fig.3).[24] Both reactions proceed in conformity with the kinetic equation (8) and have a powerful primary isotope effect[107,109,115]. The rate and selectivity of mercuration increase following the addition of $HClO_4$,[109,115] which indicates the compensation of the polar influence of the substituents. The effect of compensation is weaker than in the palladisation of arenes, because it does not lead to the reversal of the mode of substitution. This is apparently due to a weaker $d\pi-p\pi$ bonding in the π-$ArH.HgX_2$ complex as a consequence of the lower energy of the *d* electrons of mercury(II) compared with palladium(II).

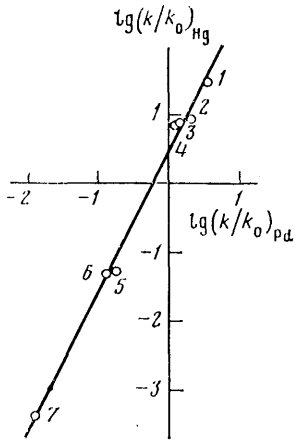
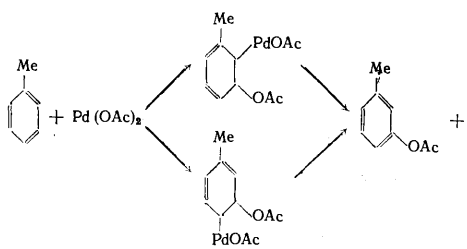


Figure 3. Relation between the rates of palladisation and mercuration of arenes in acetic acid in the presence of $HClO_4$: *1*) *o*-xylene; *2*) PhMe; *3*) PhEt; *4*) iso-PrPh; *5*) PhCl; *6*) PhBr; *7*) $PhNO_2$.[24]

The thallation of arenes probably has a similar mechanism[112,114,116]. The ratio k_H/k_D = 3.7 has been found for the reaction of $Tl(CF_3COO)_3$ with C_6H_6 and C_6D_6 in CF_3.$COOH$.[112] The electrophilic character of the metallation of arenes increases in the sequence Pd(II) < Hg(II) < Tl(III) (the corresponding values of *p* are −2.2,[24] −5.3,[115] and −7.5 [112]).

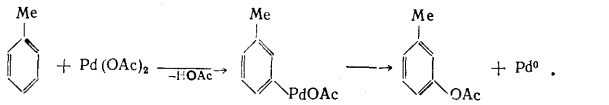
An anomalous selectivity has also been observed in the acetoxylation[51,64,89] and nitration[48,68] of arenes in the ring under the influence of palladium(II), but this phenomenon has not been attributed to electrophilic substitution in ArH. The reaction of arenes with $Pd(NO_3)_2$ in acetic acid at 90 °C involves simultaneous acetoxylation (ρ = −1.2) and nitration (ρ = −1.4). MeC_6H_4OAc and $MeC_6H_4NO_2$ with the relative proportions of isomers *meta* > *para* have been obtained from toluene. In the presence of a strong acid (Cl_3CCOOH) the acetoxylation is suppressed and the normal relative isomeric composition (*para* > *meta*) is restored for nitration, as in the oxidative coupling of arenes[68].

In order to account for the anomalous selectivity in the acetoxylation reaction, a mechanism involving the acetoxypalladisation of ArH has been proposed[51,64,89]:



(14)

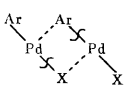
However, from the above considerations, the mechanism involving electrophilic substitution and reductive elimination is more probable for these reactions. For example, we have for *meta*-acetoxylation:



This mechanism provides a good explanation of the acceleration of the ring acetoxylation of arenes in the presence of strong oxidants[14], since they facilitate the reductive elimination from ArPdOAc as a result of the increase of the effective positive charge on the palladium atom.

It is remarkable that the hypothesis of the influence of the $d\pi-p\pi$ bonding in the arene complexes of palladium(II) on the selectivity in the coupling of arenes was already put forward in a pioneer investigation[1]. Similar ideas have received wide currency for the reactions of olefins catalysed by metal complexes[117,118]. However, the picture for the reactions of olefins is complicated as a result of the superposition on the compensation effect of the steric influence of substituents acting in the same direction. In the palladisation of arenes, the steric effects play no role for *meta*- and *para*-substitution. The conclusion that the polar influence is compensated therefore appears more justified. The unusual nature of this phenomenon from the standpoint of the general treatment of electrophilic aromatic substitution must be emphasised[90]. The use of the compensation effect to control the selectivity in the palladisation of arenes is of practical interest.

(e) *The symmetrisation of ArPdX.* The symmetrisation of ArPdX [Eqn.(9)] probably proceeds via a mechanism involving the synchronous dissociation of old bonds and the formation of new bonds in the transition state[16]



(III)

This mechanism has been proposed for the symmetrisation of stable aryl and alkyl derivatives of metals, for example ArHgX.[119]

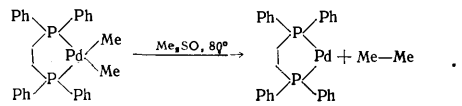
Information about reaction (9) has been obtained by analysing the distribution of aryl groups in the arene coupling products[16,88]. By analogy with the symmetrisation of ArHgX, the preferential formation of the asymmetric biaryls Ar–Ar' as a result of the synergistic effect of the Ar groups of different polarity in the transition state (III) is to be expected in the interaction of ArPdX and Ar'PdX.[119] In reality the distribution of the Ar groups in biaryls is usually close to the statistical distribution. Only in the case of very powerful directing groups ($ArNO_2$, the 2- and 3-positions in thiophen) are asymmetric biaryls formed preferentially[16,88]. This can be explained by the compensation of the polar influence of the substituents in the transition state (III) as a result of the $d\pi-p\pi$ interaction of palladium(II) with the Ar groups[88].

The distribution of the aryl groups in biaryls has been put forward as a justification of reaction (12).[22] However, in reality the available data[22] indicate a statistical distribution of the Ar groups with the exception of the coupling of nitrobenzene, for which the synergistic effect indicated above takes place[88].

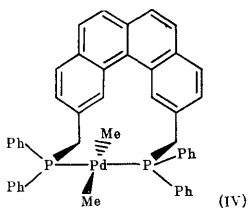
(f) *Reductive elimination.* Considerable advances have been made recently in the understanding of the mechanism of the reductive elimination of hydrocarbons from σ-diorganopalladium(II) in reactions of dialkyl and diaryl compounds of palladium(II), stabilised by phosphine ligands, taking place at a measureable rate[92–95]. These compounds are usually obtained by the oxidative addition of organic halogeno-derivatives to zerovalent palladium or by an exchange reaction:

$$ArX + Pd(PPh_3)_4 \rightarrow ArPdX(PPh_3)_2 + 2PPh_3 ,$$
$$PdCl_2(PPh_3)_2 + 2MeLi \rightarrow Me_2Pd(PPh_3)_2 + 2LiCl .$$

It has been established that palladium(II) complexes containing organic groups in the *cis*-position undergo reductive elimination[95]:



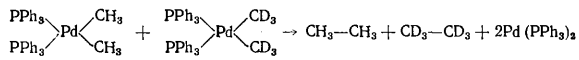
The complexes *trans*-$Me_2Pd(PPh_3)_2$ and *trans*-$Me_2Pd.(PPh_2Me)_2$ undergo the reductive elimination of ethane only after isomerisation to the *cis*-derivatives, which can be clearly observed by ^1H and ^{31}P NMR.[95] On the other hand, the complex (IV), which cannot isomerise, is stable as regards the elimination reaction.



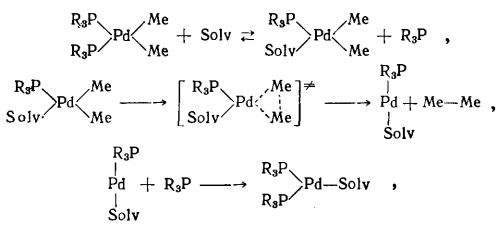
(IV)

Polar solvents [dimethyl sulphoxide (DMSO), dimethylformamide (DMF), and tetrahydrofuran (THF)] promote the elimination reaction in contrast to non-polar solvents (benzene and tetrachloroethane). The same may be said about the oxidative coupling of arenes under the influence of palladium(II). A polar solvent facilitates both *cis–trans* isomerisation of diorganopalladium(II) and the reductive elimination from *cis*-complexes [the latter via the substitution of σ-donor phosphine ligands in the coordination sphere of palladium(II), which results in an increase of the effective positive charge on the palladium ion].

The reductive elimination proceeds as an intramolecular process. This is clearly indicated by the absence of a redistribution of deuterium in the competing reaction



and by the first order of the elimination reaction with respect to diorganopalladium(II). The addition of phosphine ligands inhibits the reaction, which indicates its dissociative mechanism[95]:



where Solv is a solvent molecule.

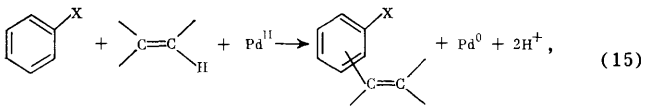
The reductive elimination is greatly accelerated in the presence of organic halogeno-derivatives capable of undergoing the oxidative addition reaction ($PhCH_2Br$, MeI, etc.). It has been suggested that in this case the elimination proceeds via palladium(IV) compounds[93–95].

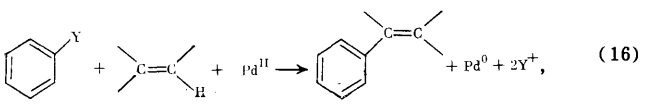
The absence of free radicals in the reductive elimination is confirmed by the retention of optical activity in α-deuteroethylbenzene obtained by the reaction of the optically active α-deuterobenzyl bromide with *cis*-$Me_2Pd(PPh_3)_2$.[93]

III. THE ARYLATION OF OLEFINS

1. General Considerations

The reaction involving the coupling of arenes with olefins, also referred to as the arylation of olefins, can be represented by the equations

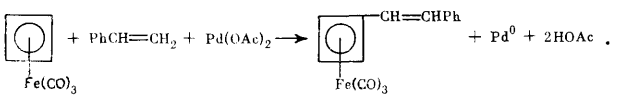

(15)


(16)

which are analogous to Eqns.(2) and (3). Here X and Y are in the main the same substituents as in reactions (2) and (3).[8,9,25,120] Reaction (15) is much faster than reaction (2) and reaction (16) is much faster than reaction (3). In the presence of olefins, biaryls are apparently hardly formed. The arylation reaction (15) is usually carried out in the presence of $Pd(OAc)_2$ in solution in acetic acid or in an arene at about 100 °C, ArH being introduced in excess relative to the olefin and palladium(II).[9] As in the coupling of arenes, reaction (16) takes place under milder conditions and more selectively than reaction (15).[25] Very effective methods have been developed using aryl derivatives of mercury(II).[25,121-123] The arylation of olefins by organosilicon compounds is promising[7].

Soluble copper(II) [25,121-124] and silver(I) [2] salts, heteropolyacids,[125] and O_2 [126] are used as oxidants in the catalytic coupling. Platinum metals on carbon are known as heterogeneous catalysts of the gas-phase arylation of ethylene[127].

The arylation of olefins is characterised by a high yield of products and a notable universality with respect to arenes and olefins. The coupling reaction takes place with aromatic carbocyclic[8,9,25] and heterocyclic[9,124,128] compounds, metallocenes[44], etc. Coordinated cyclobutadiene reacts[129,130]:



Olefins from C_2 upwards[9], cyclo-olefins[131], butadiene[123,132], alkenyl derivatives with the substituents Ar, Cl, Br, OAc, CN,[9] NO_2,[133] OR, OCOR,[122] and CH_2OH,[121] styrene, and norbornadiene in their complexes with palladium(II) [9,134], and other compounds[135,136] undergo the reaction. Acetylenes enter into an analogous reaction with formation of arylacetylenes[137].

Substituents at the double bond lower the reactivity of the olefin. In arylation by arylmercury(II) in the presence of $PdCl_2$ and $CuCl_2$ at 20 °C, the reactivity of the olefins decreases in the following sequence: ethylene (14000) > methyl acrylate (970) > propene (220) > styrene (42) > 1-methylstyrene (1).[25] The reaction is accompanied by the isomerisation with respect to the position of the double bond[25,131]. The arylation of methylolefins takes place both at the double bond of the olefin and in the allyl position[15,136].

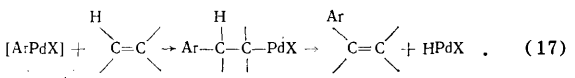
In the arylation of olefins containing an electronegative substituent (for example, a halogen) in the allyl position, aromatic allyl-substituted compounds are formed and the reaction proceeds catalytically with respect to palladium(II).[121] The arylation of olefins has a high stereoselectivity[138].

The phenylation of ethylene by benzene has been investigated as a possible method of synthesis of styrene[126,139-141]. The reaction takes place catalytically in the presence of $Pd(OAc)_2$ in benzene at 80 °C and an O_2 pressure of 10 atm.[126] However, owing to its low selectivity, it has no advantages over the traditional method of synthesis of styrene.

The selectivity in the coupling of arenes with olefins is determined by the competition with side reactions involving the oxidation, acetoxylation, and oxidative dimerisation (coupling) of olefins[126,141]. Reaction (16) of the aryl derivatives of mercury(II), tin(IV), and lead(IV) in the presence of $CuCl_2$ is accompanied by the formation of organochlorine compounds[142].

2. The Mechanism of the Coupling of Arenes with Olefins

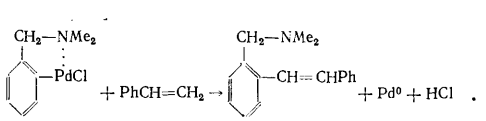
The coupling of arenes with olefins proceeds via the π–σ rearrangement of the arene and olefin π-complexes of palladium(II). Several mechanisms of the arylation of olefins have been proposed[9,10,85]. The mechanism involving the arylpalladisation of olefins and the subsequent β-elimination of palladium hydride is most thoroughly justified[10,130,134,143-149]:


(17)

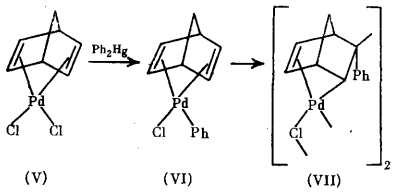
As in the coupling of arenes, the active intermediate ArPdX is formed via the electrophilic substitution in ArH, which is the rate-limiting stage of the reaction.

The arylation of olefins is accelerated by electron-donating and retarded by electron-accepting substituents in ArH. Like the coupling of arenes, the reaction has a low substrate and positional selectivity with respect to the arene as a consequence of the compensation of the electronic influence of the substituents. Thus $\lg f_p = 0.48$, $\lg (f_p/f_m) = 0.33$,[141] and $\rho = -1.4$ [130] for the reaction of toluene with styrene under the influence of palladium(II) acetate. This is consistent with the arylation of olefins via palladised ArH. At the same time the activation of palladium(II) by the olefin plays a major role in the arylation of olefins because the rate of arylation is higher by several orders of magnitude than the rate of coupling of arenes to give biaryls[85].

The involvement of ArPdX as an intermediate has been confirmed by the arylation of styrene by the palladium(II) complex of benzyldimethylamine, which has a C–Pd σ-bond:[146]



Stereochemical studies have shown that the arylpalladisation is in fact *cis*-addition[134,147]. Thus the phenylation of dichloro-η^4-norbornadienepalladium(II) by Ph_2Hg and $NaBPh_4$ in solution in CH_2Cl_2 or acetone at 20 °C gives rise to the *endo*-addition product (VII) in 79% yield:



(V) (VI) (VII)

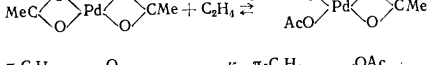
The structure of compound (VII) has been established by ^{1}H NMR and X-ray diffraction. It is suggested that the complex (VI) is an intermediate in the phenylation of compound (V); it has been possible to isolate its stable platinum analogue[134].

The *cis*-addition of ArPdX to the double bond of the olefin is controlled to a greater extent by steric factors than electronic factors[143]. The compensation of the electronic effects of the substituents in the olefin in its π-complex with ArPdX prior to the arylpalladisation reaction (17) probably plays an appreciable role in this process. A large organic group usually adds contrary to the Markovnikov rule, to the least substituted carbon atom involved in the double bond, while palladium(II) adds to the most substituted carbon atom. Thus the phenylation of propene by PhHgOAc in the presence of palladium(II) acetate in acetic acid yields 70% of 1-phenylprop-1-ene, 14% of allylbenzene, and 16% of 1-methylstyrene, i.e. the ratio of the yields of the products of the addition of PhPdOAc to the terminal and inner carbon atoms of propene is 5.3.[143] A similar result was obtained in the phenylation of propene by benzene[141].

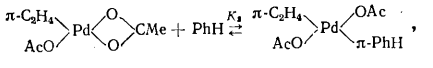
The phenylation of olefins (Ol) under the influence of the monomeric $Pd(OAc)_2$ complexes in benzene proceeds in accordance with the kinetic equation

$$W = k\,[Pd(OAc)_2]\,[Ol]\,[PhH]\ . \qquad (18)$$

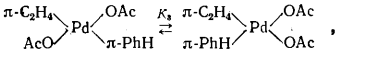
For the reactions of ethylene and styrene, the values of $k[PhH] \times 10^3$ are respectively 2.2 and 0.196 $mol^{-1}\ s^{-1}$ at 95 °C. For the reaction of ethylene, E = 68.7 kJ mol^{-1}.[141,145] The phenylation of styrene and ethylene by benzene and deuterobenzene-d_6 is characterised by the kinetic isotope effect k_H/k_D = 5.0; for the reaction of C_2D_4 and styrene-β,β-d_2 with benzene, k_H/k_D = 1.2. The isotope effects in the reaction rates and products are the same[141,144,145]. Taking into account these data, the mechanism of the arylation of olefins by the monomeric $Pd(OAc)_2$ in benzene has been represented as follows[144,145]:



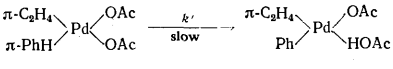
(19)



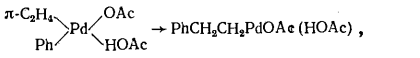
(20)



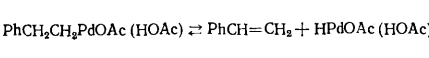
(21)



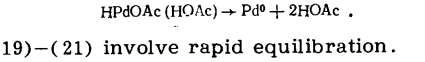
(22)



(23)

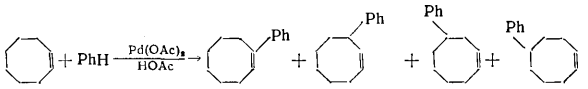


(24)

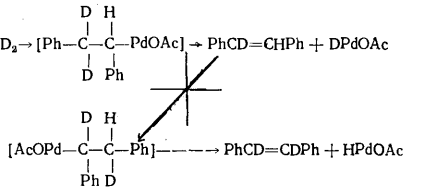


(25)

Stages (19)–(21) involve rapid equilibration. The coordination of the olefin facilitates the partial substitution of the bidentate acetate ion in the *trans*-position by an arene molecule as a consequence of the strong *trans*-effect of the olefin. The isomerisation [reaction (21)] to the favourable *cis*-configuration can proceed via the five-coordinated intermediate as a result of the addition of a second phH molecule[74,75] or with participation of the bidentate acetate ion. The rate-limiting stage (22), analogous to reaction (13), involves the π–σ rearrangement of the arene in the coordination sphere of palladium(II). It is irreversible because there is no H–D exchange between ArH and the solvent in the arylation of olefins[144]. There is a probability of proton transfer to the ligand in the reaction in benzene; in more basic media, the solvent may be the proton acceptor (see above). Since the introduction of additional π ligands into the coordination sphere of the metal ion promotes the π–σ rearrangement as a result of the destabilisation of the existing π ligands[19], the higher rate of arylation of olefins compared with the coupling of arenes to biaryls becomes understandable[141]. The *cis*-arylpalladisation stage (23) is apparently rapid and irreversible. In the general case the β-elimination reaction (24) is fast and reversible[131,143], as shown by the isomerisation of the products of the arylation of cyclo-olefins via the repeated addition-elimination of palladium hydride[131]:



However, in the arylation of styrene stage (24) is almost irreversible, which is confirmed by the absence of a hydride shift in the reaction of styrene-β,β-d_2:[128,148]



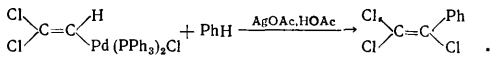
The kinetic equation

$$W = \frac{k'K_1K_2K_3\,[Pd(OAc)_2]\,[Ol]\,[PhH]}{1 + K_1[Ol]\,\{1 + K_2[PhH]\,(1 + K_3)\}}\ ,$$

which is the same as Eqn.(18) for $K_1[Ol]\{1 + K_2[PhH].(1 + K_3)\} \ll 1$, where $k = k'K_1K_2K_3$, follows from reactions (19)–(25).[141,145] The olefin activity series obtained C_2H_4 > $PhCH=CH_2$ [141,145] is consistent with the sequence of the stabilities of the π-complexes of olefins with palladium(II) acetate[76].

The trimer $Pd_3(OAc)_6$ and the dimer $Na_2Pd_2(OAc)_6$ are active in the arylation of olefins in acetic acid[85]. The kinetics of the arylation of olefins in acetic acid under the conditions of the association of palladium(II) acetate are more complex than the kinetics of the reaction with monomeric $Pd(OAc)_2$ in benzene and depend significantly on the nature of the arylating agent. The phenylation of styrene by benzene in acetic acid is of zero order with respect to the olefin and of first and 0.5 order with respect to the palladium(II) acetate dimer and trimer respectively. The dependence of the rate on the concentration of PhH is consistent with the Michaelis equation, which indicates the formation of π-arene complexes of palladium(II). The arylation of styrene by naphthalene and PhHgOAc proceeds via two parallel pathways of zero and first order with respect to the olefin. In order to account for these data, a mechanism involving the oxidative addition of ArH to palladium(II) has been proposed at the rate-limiting stage[85,150]. However, one cannot rule out the possibility that the process may be limited by the dissociation of polymeric palladium(II) species under the influence of ArH to give more active monomeric palladium(II) complexes.

It is of interest that the arylation of olefins can be carried out with participation of σ-vinyl complexes of palladium(II):[9]

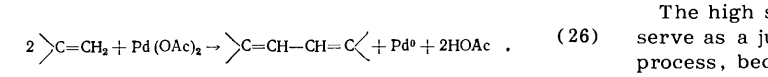


However, this mechanism has no general importance. This is demonstrated by data concerning the oxidative dimerisation of α-olefins to 1,3-dienes which proceeds via σ-vinyl derivatives of palladium(II) (see below). Since ethylene and linear olefins do not enter into this reaction, there is no reason to assume that their arylation proceeds via σ-vinylpalladium(II) compounds. Furthermore, the stage involving the substitution of the vinyl hydrogen atom by palladium(II) should be partily reversible, since it precedes the rate-limiting stage in which ArH is palladised. However, this is inconsistent with the absence of H–D exchange between olefins and the solvent under the conditions of the arylation reaction[128,148].

IV. THE OXIDATIVE COUPLING OF OLEFINS

1. Conditions and Products of the Reaction

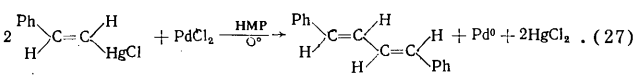
The coupling of olefins (another commonly used term is oxidative dimerisation) takes place in solutions of palladium(II) salts, usually $Pd(OAc)_2$, with formation of derivatives of 1,3-dienes:[3,151,152]



(26)

Olefins substituted at the double bond, for example, styrene, 1-methylstyrene, 1,1-diphenylethylene, vinyl acetate, etc., undergo this reaction[151,152]. Ethylene, the β-unbranched olefins $R-CH_2-CH=CH_2$, and β-chloroolefins are inactive. The coupling is exclusively of the "head to head" type, i.e. a C–C bond involving the least substituted carbon atoms of the double bonds is formed[152].

Alkenylmercury(II) derivatives, obtained by the addition of mercury(II) salts to acetylenes, undergo stereospecific coupling under the influence of $PdCl_2$:[153]



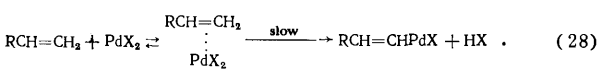
(27)

In the presence of copper(II) and iron(III) salts[154] or oxygen[126], reaction (26) takes place catalytically. Both homogeneous[126] and heterogeneous[155,156] catalysts based on palladium compounds are known.

The oxidation and acetoxylation of olefins[3,126,141] as well as their non-oxidative dimerisation[5] compete with the coupling of olefins. In the presence of arenes, olefins are arylated[141].

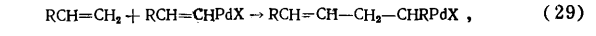
2. The Mechanism of the Coupling of Olefins

The available experimental data can be generalised within the framework of the hypothesis that the oxidative coupling of olefins proceeds via a slow π–σ transformation stage with formation of vinylpalladium(II) derivatives[5,10,14,157]:

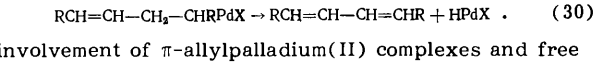


(28)

Next, as in the non-oxidative dimerisation of olefins[117,158], rapid insertion of the olefin in the C–Pd bond and β-elimination of palladium hydride take place[5,10,157]:

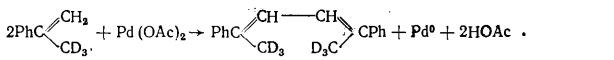


(29)

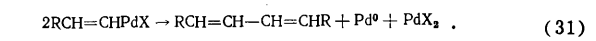


(30)

The involvement of π-allylpalladium(II) complexes and free radicals is ruled out in view of the high selectivity of the "head to head" coupling and the retention of deuterium in the products of the coupling of 1-methyl-d_3-styrene:[152]



A disproportionation reaction, analogous to the sum of reactions (9) and (10) for the coupling of arenes, has been proposed as a second pathway leading to the formation of the C–C bond[10,14,157]:



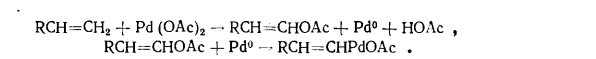
(31)

Reaction (27) of vinylmercury(II) derivatives confirms the possibility of such a pathway. However, stage (29) is more probable in the coupling of olefins. It should be fairly rapid, because it is an analogue of the chain propagation stage in the Ziegler–Natta polymerisation[117,158]. The occurrence of reaction (29) is promoted by the condition $[RCH=CHPdX] \ll [RCH=CH_2]$. An example of the faster insertion of an olefin in the C–Pd bond compared with the disproportionation of the σ-organopalladium(II) may be provided by the arylation of olefins, since biaryls are hardly formed in this reaction. The involvement of stage (29) in the coupling of olefins is also confirmed by the formation of non-oxidative dimerisation side products[5,141].

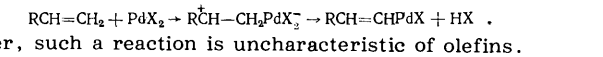
The high selectivity of the "head to head" coupling cannot serve as a justification of the involvement of stage (31) in the process, because, as mentioned above, the insertion of olefins in the C–Pd bond is subject to rigid steric control[138,143]. Furthermore, examples are known of non-oxidative "head to head" dimerisation of olefins catalysed by palladium(II) complexes with nearly 100% selectivity[158].

The mechanism (28)–(30) has been confirmed by kinetic data. Polymeric forms of palladium(II) acetate are active in the oxidative dimerisation of styrene in acetic acid: $Pd_3(OAc)_6 > Na_2Pd_2(OAc)_6 \gg Na_2Pd(OAc)_4$. The reaction is of first order with respect to the palladium(II) acetate dimer and trimer and in the latter case also of first order with respect to the olefin[157]. The formation of fairly stable π-complexes $Na_2Pd_2(OAc)_5(Ol)$ in a system containing $Na_2Pd_2(OAc)_6$ has been demonstrated by kinetic and spectroscopic methods[76,157].

The detailed mechanism of the π–σ reaction (28) has not been elucidated. The reaction is irreversible, because the products of the oxidative dimerisation of olefins in DOAc do not contain deuterium[152]. It has been suggested that the vinylpalladium(II) derivative is formed via the acetoxylation of the olefin and subsequent oxidative addition of alkenyl acetate to zerovalent palladium[5]:

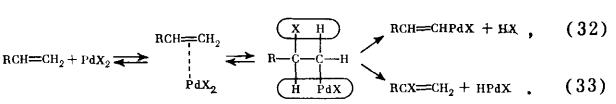


A scheme has been proposed for the direct electrophilic substitution of vinyl hydrogen by palladium(II), by analogy with the palladisation of arenes[14,157]:



However, such a reaction is uncharacteristic of olefins.

The electrophilic substitution of vinyl hydrogen via an addition–elimination mechanism is more probable[141]:



(32)

(33)

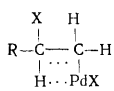
(VIII)

This mechanism agrees well both with oxidative dimerisation data and with the general ideas concerning the reactivity of olefins. The addition of PdX_2 in accordance with the Markovnikov rule leads to the coupling of olefins; otherwise, acetoxylation takes place. The probability of the latter is evidently smaller for β-disubstituted olefins as a consequence of the concerted steric and electronic influence of substituents in the olefin. β-Unbranched olefins are inactive in oxidative dimerisation, probably as a consequence of their acetoxylation in the allyl position and the formation of inert π-allyl-palladium(II) complexes. β-Chloro-olefins are apparently preferentially acetoxylated via the elimination of palladium chloride.

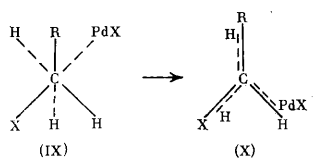
The addition of palladium(II) to olefins is reversible. This is indicated by the catalysis by palladium(II) compounds of reactions such as the transesterification of vinyl esters of carboxylic acids[159], the isotope exchange of chloride ions between $Li^{36}Cl$ and vinyl chloride[160], the isomerisation of *trans*-ethylene-1,2-d_2,[161] etc. The acetoxypalladisation of olefins in acetic acid solution proceeds via the *trans*-attack on the olefin by a solvent molecule[14].

The elimination from the intermediate (VIII) takes place via the two competing reactions (32) and (33). Reaction (32), which leads to the formation of vinyl-palladium(II), belongs to the class of the well known olefin 1,2-elimination processes in which the mode of substitution and the effects of substituents have been investigated in detail[90]. For X = OAc, the 1,2-elimination of olefins usually proceeds via a bimolecular E2 mechanism involving the synchronous removal of X^- and proton transfer to a base, which may be a nucleophilic solvent[90]. The influence of the substituent R on the rate of reaction (32) is determined by its inductive and mesomeric effects; steric effects do not usually play a significant role. The introduction of alkyl substituents in the α-position relative to X accelerates reaction (32). The effect of α-aryl substituents is much stronger; they promote reaction (32) as a result of conjugation with the double bond formed in the transition state[90].

The β-elimination of palladium hydride [reaction (33)] probably takes place intramolecularly via a cyclic transition state[117]:



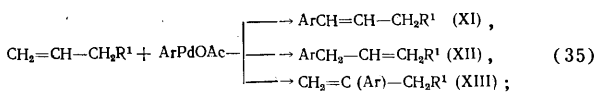
The activation process apparently involves the transition of the system from a more stable inhibited conformation, for example, of type (IX), to the eclipsed conformation (X):



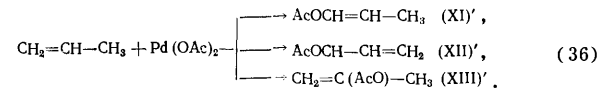
(34)

(IX) (X)

The mode of substitution and the effect of substituents in the β-elimination of palladium(II) hydride have been hardly investigated although they are undoubtedly of great interest. Certain conclusions can be reached from data concerning the products of the reactions involving the arylation and acetoxylation of olefins considered below, which have been studied in detail under conditions which rule out the migration of the double bond[78,138,143]:

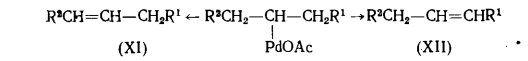


(35)



(36)

The ratio of the products (XI) and (XII) [and correspondingly (XI)′ and (XII)′] yields information about the influence of the nature of the substituents in the β-position relative to palladium(II) on the mode of β-elimination of HPdOAc:



(XI) (XII)

These data are presented in Table 2. In the first place it is seen that the polar influence of the substituents on the β-elimination of HPdX agrees with the fact that in this reaction hydrogen is split off from the carbon atom in the form of the hydride ion and palladium is split off in the form of XPd^+. Thus electron-accepting substituents hinder the abstraction of an α-hydrogen atom, while electron-donating substituents facilitate it [cf. R^1 = OAc or CN and R^2 = Ph, R^1 = H and R^2 = *p*-$MeOC_6H_4$, Ph, or *p*-$AcOC_6H_4$, and R^1 = H or n-Pr and R^2 = Ph in reaction (35)]. In these series the steric effects of the substituents R^1 and R^2 are either of the same order of magnitude or do not change when the substituents are varied. The data for reaction (36) permit the same conclusion, although here the role of the steric factors may prove to be more significant. This is indicated by the dependence of the yields of the products (XI)′ and (XII)′ on the sodium acetate concentration, which determines the degree of association of palladium(II) acetate (see Section II, Subsection 2). The mode of elimination of palladium hydride is influenced by both the inductive and mesomeric effects of the substituent. The aryl group promotes the formation of a double bond which is conjugated with it. The directing effect of the aryl group is much stronger than that of the alkyl group (see R^1 = n-Pr, R^2 = Ph).

Table 2. The mode of β-elimination of palladium hydride in olefin arylation and acetoxylation reactions under the influence of palladium(II) acetate.

Reaction*	R^1	R^2	Relative contents, %		
			XI, (XI),	XII, (XII),	XIII, (XIII),
(35)	H	*p*-$MeOC_6H_4$	53	4	43
(35)	H	Ph	62	12	26
(35)	H	*p*-$AcOC_6H_4$	58	18	24
(35)	n-Pr	Ph	47	7	18
(35)	CN	Ph	45	0	0
(35)	OAc	Ph	94	0	5
(36)	H	OAc	2	2	96
(36) **	H	OAc	0.5	13	86.5
(36) ***	H	OAc	3	71	26
(36) ****	H	OAc	<0.5	94	2

*Reaction (35)—in acetonitrile at 20–30 °C;[138] reaction (36)—in acetic acid at 25 °C.[78] The reactions were carried out in the absence of chloride ions; there is then no migration of the double bond.

**[NaOAc] = 0.098 M.

***[NaOAc] = 0.49 M.

****[NaOAc] = 0.90 M.

It follows from the foregoing that the electronic effect of the substituent R acts in the same direction on reactions (32) and (33) and apparently does not affect their competition.

However, the steric effect of R differentiates these reactions. As already mentioned, the steric factor usually does not play a significant role in reaction (32). On the other hand, in the β-elimination of HPdX the rate of the activated process (34) depends greatly on the bulk of the substituent R. For bulky substituents, for example Ar, the formation of the eclipsed conformation (X) is difficult and reaction (32), leading ultimately to the olefin coupling products, therefore take place preferentially. For β-disubstituted olefins, reaction (33) is altogether ruled out. Thus the addition–elimination mechanism (32) and (33) is fully consistent with the experimental data on the coupling of olefins.

In conclusion one should note that the oxidative coupling reactions of unsaturated hydrocarbons under the influence of palladium(II) compounds have common fundamental elements in their mechanisms. They all proceed via a sequence of $\pi-\sigma$ reactions in the coordination sphere of palladium(II) and include the electrophilic substitution of hydrogen by palladium(II) at a trigonal carbon atom as the rate-limiting stage. The intermediate $d\pi-p\pi$ binding of palladium(II) as a "soft" acid to "soft" bases (arenes of olefins) plays an important role in these reactions. As a result of this, the mode of palladisation of the substrate is inconsistent in many instances with the traditional ideas concerning the ratio of the electronic and steric factors in reactions of unsaturated hydrocarbons with electrophiles. This phenomenon is of significant interest for metal complex catalysis as a method of controlling the selectivity of reactions and merits detailed study.

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Steric Aspects of the Formation of Metal Chelate Complexes

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The geometrical and thermodynamic aspects of the formation of complexes between metal cations and organic ligands are examined theoretically from the standpoint of conformational analysis. Particular attention has been devoted to the problem of the selectivity of the complex formation, which is of practical importance. It is shown that the selectivity of complex formation is largely determined by the steric factor. The advantages and disadvantages of the available methods for the quantitative allowance for the steric factor as well as methods of calculation of the structure of coordination compounds are analysed.
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I. INTRODUCTION

The problems of the stability of metal complexes and the selectivity of complex formation are of central importance in coordination chemistry, particularly in the chemistry of complexones and extractants. Universal complexones, which are capable of binding effectively to the majority of cations in solution (in a specific pH range), have been synthesised on the basis of iminodiacetic, ethylenediaminetetra-acetic, and a number of other acids[1-3]. By virtue of their flexibility and multidentate nature, the molecules of these acids can form complexes with cations of different size. However, much more attention has been devoted recently to the synthesis of highly selective reagents capable of the selective chelation of specific cations. Numerous applications are associated with the synthesis of such reagents: in atomic industry and hydrometallurgy (extraction and separation of rare metals and radioactive isotopes), in medicine and pharmacology (the elimination from the organism of harmful metals, particularly radioactive metals, and the introduction into the organism of the essential metals—for example, iron in iron-deficiency anaemia), and in chemical industry and catalysis (the formation of complexes with a specified steric structure and with a specified stability in a particular medium).

The free energy of the binding of the metal to the ligand under specified external conditions (solvent, temperature, etc.) depends both on the metal–donor centre bond energy and on the steric structure of the ligand. In many instances of practical importance the variations in the metal–ligand donor centre bond energy are either small or are comparatively easy to take into account quantitatively. The most important factor determining the selectivity of the ligand therefore becomes its steric structure (conformation).

This review is devoted to the consideration of the influence of the ligand conformation on the selectivity of the complex formation and also of the methods for the theoretical study of the conformational possibilities and the steric structure of metal complexes. Its aim consists in summarising the hitherto few investigations in this field and in assessing the likely usefulness of the theoretical approaches to the prediction of the structures of ligands exhibiting a specified selectivity with respect to particular metal cations.

II. THE STERIC FACTOR IN COMPLEX FORMATION

1. Thermodynamic and Geometrical Conditions Governing Complex Formation in Solution

We shall consider initially certain questions of the thermodynamics of complex formation[4]. Bearing in mind that the reactions take place in solution, we can write

$$M_s^+ + L_s \rightleftarrows (ML')_s \qquad (1)$$

where M^+ is the metal cation, L the ligand, and (ML') the complex formed; the prime denotes that, as a result of its interaction with the cation, the ligand can undergo a change in its conformation, while the subscript s denotes the solvated state. In the general case L can have an integral coefficient; in addition, one cannot rule out the possibility of the addition of several different ligands to the cation.

Eqn.(1) can be given the following simple significance: the formation of the complex is equivalent to the replacement of the solvation shell and the new shell of the cation consists of the ligand molecules, which are in their turn solvated. When the free energy ΔF of the forward process in reaction (1) is negative, the equilibrium is displaced to the right, i.e. the formation of the complex is favoured by free energy factors; on the other hand, if $\Delta F > 0$, the equilibrium is displaced to the left.

In order to consider reaction (1) further, we shall divide it into several hypothetical elementary processes whose thermodynamics can be investigated in principle:

$$M_s^+ \rightleftarrows M^+, \qquad (I)$$

$$L_s \rightleftarrows L, \qquad (II)$$

$$L \rightleftarrows L', \qquad (III)$$

$$M^+ + L' \rightleftarrows (ML'), \qquad (IV)$$

$$(ML') \rightleftarrows (ML')_s. \qquad (V)$$

Processes (I) and (II) correspond to the desolvation of the cation and the ligand and are accompanied by a considerable increase of the free energy of the system ($\Delta F_1 > 0$ and $\Delta F_2 > 0$; here and henceforth we speak of the free energies of the forward processes). Process (III) is also

energetically unfavourable, because generally speaking the ligand molecule must undergo a change in its conformation on approaching an ion having a particular radius†. The free energy gain in the first three stages is compensated by energy factors favouring the formation of coordinate bonds [process (IV)] and the solvation of the complex [process (V)]. Ultimately we have for the overall process

$$\Delta F = \sum_{i=1}^{5} \Delta F_i$$

and

$$K_M^{ML} = [ML]/[M]\cdot[L] = \exp(-\Delta F/RT) \quad .$$

If equilibrium (1) is displaced to the right, one can write

$$|\Delta F_4 + \Delta F_5| > |\Delta F_1 + \Delta F_2 + \Delta F_3| \quad .$$

It is significant that the hypothetical processes (III) and (IV) are gas-phase reactions. In the calculation of ΔF_3, one can therefore use the classical methods of conformational analysis based on the model of atom–atom potential functions[5] and the influence of the solvent can be disregarded. The greatest and approximately equal in absolute magnitude are the contributions ΔF_1 and ΔF_4, which amount to $\sim 10^2$–10^3 kJ mol^{-1} and have the opposite signs. Complex formation therefore resembles a replacement of the solvation shell of the cation when it is transferred from one solvent to another with a greater solvating capacity (for example, from alcohol to dimethylformamide).

A rigorous estimation of all the contributions to ΔF requires the knowledge of the potential surfaces of the interactions of the cations, ligands, and complexes with the solvent molecules and also of the cations and ligands with one another. However, even if one imagines that such surfaces have been obtained with the aid of non-empirical calculations, the extremely complex problem of the statistical-mechanical averaging of thermodynamic functions with respect to the microstates of the system still remains. Various approximate approaches, postulating certain relations between the contributions to ΔF for specific series of ligands and cations, are therefore of interest[4]. One can imagine a situation where such relations permit the calculation of the stability constants of the complexes K_M^{ML} solely on the basis of the calculated ΔF_3 (naturally a particular model of the solvation shell must be selected for this purpose[6]).

In considering the geometrical aspects of complex formation, one may isolate three different levels of theoretical studies, each of which yields useful information about the structure and energetics of coordination compounds.

1. The study of the geometrical stabilities of isolated ligands, i.e. their theoretical conformational analysis.
2. The search for the possible distribution of the ligand donor atoms on the sphere of the central ion.
3. The study of the interaction of atoms in the complex not linked by valence bonds: (a) in chelate rings; (b) between different rings (for example, in the case of two or three bidentate ligands); (c) between chelate rings and solvent molecules (with partial retention of the solvation shell).

†Complex formation is not always accompanied by an appreciable alteration of the ligand conformation; for example, there is a possibility of the capture of a metal cation on rupture of intermolecular hydrogen bonds without significant changes in various geometrical parameters of the ligand. However, even then, by taking into account the energy of hydrogen bonding, one may speak of a contribution ΔF_3.

We shall consider each of the levels enumerated. Theoretical conformational analysis of the ligand makes it possible to discover, in principle, whether the given ligand forms a ring with the metal ion and which ions are preferable in this sense. In a macrocyclic complex one can investigate the question of the minimum and maximum sizes of the cavity. Ligands whose potential surfaces are characterised by a deep minimum corresponding to the conformer capable of binding ions with a specific radius are evidently highly selective. The selectivity of such systems is associated with the rigidity of the ligand.

If the rigidity of a bidentate ligand is defined in terms of the distance between the donor atoms, then the shorter the range within which this distance varies, the more effective the "approach" or "its failure" to the "claws" by an ion having the specified radius. This is illustrated in Fig.1, where $R_{L\ldots L}$ denotes the distance between the donor atom and the ligand calculated theoretically, l the length of the coordinate bond, and θ the LML angle. For alkali metal ions, the bond length l has been shown by experimental data to be approximately equal to the sum of the van der Waals radius of the donor atom and the crystal-chemical radius of the ion; for other metals, particularly transition metals, this bond is in general somewhat shorter (to a first approximation, its length can be assumed equal to the sum of the covalent radii of the metal and the donor atom) and can be obtained from crystal-chemical data.

It is readily seen that

$$R_{L\ldots L} = 2l\sin(\theta/2) \qquad (2)$$

or, if it is assumed that $l = R_0 + R_M$ (where R_0 and R_M are the van der Waals and crystal-chemical radii), which is usually the case for ionic bonds, we obtain

$$R_M = R_{L\ldots L}/2\ \sin(\theta/2) - R_0 \ . \qquad (3)$$

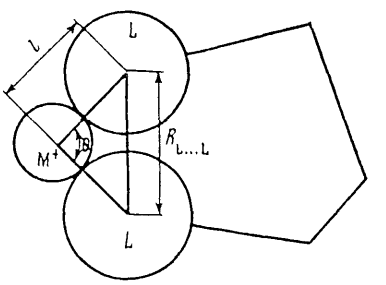


Figure 1. Schematic illustration of the formation of a chelate ring.

Eqn.(3) shows that even an absolutely rigid ligand does not determine the radius of the metal ion unambiguously; the angle θ is also significant. For octahedral or square coordination, the values of θ are close to 90°. However, it is also necessary to take into account the possibility of the deformation of θ (according to X-ray diffraction data for metal complexes, the experimental θ are in the range from 75° to 95°). If only one bidentate ligand is involved in the complex formation and the remaining sites in the octahedron (which is generally speaking distorted) are occupied by the

donor atoms of the solvent molecules, then θ should approach 90°. This happens also in the square coordination; in tetrahedral coordination the angle θ is known to be close to 109°.

In the analysis of complex formation between polydentate (in particularly macrocyclic) ligands and metal cations, the scheme in Fig.1 is unsuitable and a more detailed approach is necessary. In this instance it is apparently essential to find the optimum position of the cation by minimising the sum $\sum_i (l_i - l_0)^2$ (where l_i are the calculated cation–donor atom distances and l_0 is the "ideal" length of the coordinate bond). If the sum remains fairly large after minimisation, then the formation of a complex is not favoured. Naturally, the optimisation procedure must be carried out for each conformation of the macroring corresponding to a fairly low energy.

The approach to the analysis of the complex formation geometry examined above is not of course the only one possible. Thus, in the chemistry of metal complexes having monodentate phosphorus ligands, the "steric parameter" θ, equal to the solid angle formed by the van der Waals spheres of different substituents at the phosphorus atom, is widely used[7]. If the Stewart–Briegleb models of ligands such as $P(OCH_2)_3CMe$, PMe_3, $P(OPh)_3$, PPH_3, P(cyclohexyl)$_3$, and P(t-Bu)$_3$ are assembled, it becomes clear that the solid angle diminishes in this series (in the case of the asymmetric ligand $PX_1X_2X_3$ the parameter θ is defined as the sum of the contributions θ_i of each X_i). Consequently the ability of phosphorus-containing ligands to form complexes with metals must fall within the above series, which is in fact observed experimentally. However, it is difficult to assess the energetics of the complex formation on the basis of the steric parameter θ.

In the next level of theoretical studies of the steric structure of coordination compounds, one can consider the interaction of the donor atoms of ligands on the sphere of the central ion (see Section IV). For this purpose, one may employ the approach, developed by Kepert[8,9], which resembles the familiar Gillespie–Nyholm "points on a sphere" theory[10] and in our case the points are not electron pairs as in Gillespie's book[10] but the donor atoms of the ligands, whose positions on the sphere of the central ion are optimised. The optimum structure of the complex and the relative stabilities of the different coordination polyhedra must evidently depend on the radius of the ion, the size of the donor atoms (or the adjacent polyatomic groups), and the number of binding sites of the ligand. Calculations within the framework of the models for the interaction of donor atoms considered below permit, firstly, the prediction of the type of polyhedron for the given coordination compound and, secondly, the selection of the starting point for the minimisation of the energy of the complex.

In the third level of investigations, as in the first, the calculations are performed within the framework of the model of the atom–atom potential functions, but here one takes into account not only the interactions within the chelate rings but also the "intermolecular" interactions between them and the interactions with the solvent molecules involved in the coordination. Conformational studies on complexes of certain transition metals with alkylenediamines and some aminoacids, which belong to the third level within the framework of the scheme considered here, have been frequently carried out by different investigators (see, in particular, the careful review by Hawkins[11]). However, the problem of the logical analysis of the steric effects with determination of the principal factors governing the stability of the complexes in solution was apparently formulated only a few years ago[4].

2. Methods for the Calculation of the Conformational Energy and Entropy of Ligands

We shall consider the problem of the conformational analysis of isolated ligands. The task is to calculate the energy as a function of independent geometrical parameters, i.e. to obtain the potential surface and to find on the latter the energy minima corresponding to stable conformers. Such information can be provided, in principle, by quantum-chemical methods—both non-empirical and semi-empirical. Taking into account the fact that the potential surfaces of metal complexes with organic ligands as well as the surfaces of the ligands themselves are multidimensional and "have many extrema", one of the requirements which must be met by the method for their investigation is a not unduly long time for machine computation of the energy. This requirement is satisfied most effectively by the method of atom–atom potential functions (AAPF) and it is not surprising that this is in fact used in the vast majority of calculations. According to the AAPF method, the energy of the molecule is represented by the sum of the contributions of non-valence, torsional, and electrostatic interactions as well as the energy of the deformation of the valence bonds and angles:

$$U_{\text{non-}\sigma} + U_{\text{tors}} + U_{\text{el}} + U_{\text{bond}} + U_{\text{angle}} \ .$$

The parameters of the potential functions have been discussed in a series of reviews[5,12–15], in particular the parametrisation for the calculations of the conformations of metal complexes has been examined[11,15]. We shall therefore consider only certain features associated with the application of the AAPF method to the conformational analysis of complexes and ligands.

As regards the parameters of the potentials of the non-valence interactions (the Lennard-Jones or Buckingham potential), the spectra of their values used by different workers are so broad that, within the framework of this review, we are unable to discuss this question in any detail. Thus modified Hill potentials[19] (p.529) have been used in the pioneer studies of Gollogly and Hawkins[16–18], who were the first to estimate the conformational energies of chelate rings. De Hayes and Busch[20,21], who calculated the conformations of five- and six-membered rings in compounds of the type M(L)Cl$_4$, where M is the metal atom [cobalt(III)] and L is ethylenediamine, trimethylenediamine, etc., using Allinger's parametrisation[22,23]. Niketić and Woldbye[24,25], who investigated trisdiamine complexes of cobalt(III), used two sets of constants for the Buckingham (6-exp) potential—those of Liquori and coworkers[26,27] and Ramachandran et al.[28]—and showed that both sets lead to approximately identical results. Finally the potentials of Scott and Scheraga[29] or Dashevskii[30,31] are most often used in the conformational analysis of peptide and depsipeptide macrocyclic complexes. We may note that all the sets of parameters of the atom–atom potentials are concerted (with the possible exception of the Liquori potential) and give rise to a good accuracy of the calculation of the conformational energies. The only important feature is that these potentials should be applied together with the corresponding sets of angular and torsional constants, since otherwise the calculation can lead to serious errors (for example, the use of the Allinger potentials requires the neglect of the 1...3 interactions and the use of spectroscopic constants for the valence angles).

The choice of the energy barrier U_0 in the expressions for the torsional potentials involves certain difficulties. Whereas the majority of investigators agree on the value $U_0 \cong 10$–12 kJ mol^{-1} for saturated C–C bonds, the values

of U_0 adopted by different investigators for bonds with a nitrogen atom and in particular for the Co–N bond in classical ethylenediamine complexes diverge significantly. It is therefore necessary to investigate the question of the influence of the uncertainty in the form of the torsional potential and in the value of U_0 on the principal calculated results, for example, on the calculated relative stabilities of the conformers. This is also true of the electrostatic component of the potential energy function (although the majority of workers who have calculated the conformations of the classical complexes were able to disregard it). The errors introduced by this component are associated with the uncertainty in the choice of parameters (the charges and the value of ε, present in the denominator of the expression for Coulomb's law and defined as the effective dielectric constant of the medium).

In the conformational analysis of ligands, the deformation energies of the valence angles and bonds can be neglected in most cases. However, when chelate rings are considered, these terms of the potential function are significant. Without taking into account the deformations of the valence angles, it is hardly possible to predict correctly the geometries and relative stabilities of different spatial isomers of involved complexes with two or three chelate rings. An important variable is also the length of the coordinate bond l. The analysis of the results of the X-ray diffraction of numerous octahedral complexes leads to the conclusion that the lengths l are minimum when $\theta = 90°$ (see Fig.1); on the other hand, when the angles θ are distorted, the increase in the length of the coordinate bond can actually exceed 0.01 nm.

The search for the optimum (or simply the stable) conformation of the complex involves the minimisation of the potential energy with respect to independent geometrical parameters, which is carried out for a specified zeroth approximation. Buckingham and coworkers[15], Busch[20], and certain other investigators have used in their calculations Boyd's program[32] based on the Newton–Raphson method and requiring the calculation of second derivatives. The advantage of this program consists in the fact that, simultaneously with the choice of direction of the one-dimensional descent, the computer yields information also about the normal vibration frequencies. In a number of other studies[24,25] the potential energy minimisation procedure was based on Wiberg's algorithm[33], the idea of which consists in selecting the direction of descent on the basis of first derivatives; the independent geometrical parameters are then the cartesian coordinates of the atoms. From our point of view, neither algorithm is entirely successful: the first requires a large amount of calculations in order to obtain the second derivatives of the conformational energy with respect to independent parameters and the second converges much too slowly near the potential minimum (furthermore, when the cartesian coordinates of the atoms are chosen as the independent variables, the function is found to be relatively insensitive to the angles of rotation). The Fletcher–Powell and parallel tangent methods as well as certain others are more successful (they are discussed by Dashevskii[5]); they do not require the calculation of second derivatives but exhibit second order convergence.

The minimisation of the potential energy with respect to independent geometrical parameters leads to the optimum geometry of the isolated ligand and yields the energy E_0 corresponding to this geometry. On the other hand, if the minimisation is carried out for a fixed value of $R_{L\ldots L}$, it is possible to estimate the energy E' of the deformed ligand (the deformation is associated with the formation of a chelate ring) and to calculate $\Delta E_3 = E' - E_0$, i.e. the contribution of the potential energy to process (III). However, this is still insufficient to estimate the contribution ΔF_3, because the calculations based on the minimisation of the conformational energy do not take into account the entropy factor.

It is noteworthy that chelation is generally speaking unfavourable on entropic grounds (naturally if no account is taken of translational entropy), since it inevitably involves the loss of one or several degrees of freedom by the ligand. The magnitude of this effect naturally depends on the conformational freedom of the isolated ligand: if the formation of coordinate bonds leads to the generation of one of a multiplicity of the possible conformers which in addition has a wide probability distribution (the potential surface of the ligand has several minima and/or these minima are fairly broad), then the free energy gain on chelation may be so large that the entropy factor is in fact the main one in determining the stability of the given complex in a certain series; on the other hand, if the ligand is fairly rigid in the isolated state, then complex formation does not alter the entropy of the system seriously.

This factor has been noted by many workers[34–38], but the methods for taking into account the entropy remained for a long time far from perfection. The first semi-quantitative estimates of the entropy of chelation were made by Westheimer and Ingraham[39], who calculated the translational entropy on substitution of two monodentate ligands by a single bidentate ligand and also the entropy of cyclisation due to the "freezing out" of internal rotations. Their main result[39] reduces to the fact that the increase of translational entropy as a result of the liberation of two solvent molecules on binding only one ligand molecule is compensated by the decrease of entropy associated with the freezing out of the internal rotations in five- and six-membered rings. However, this compensation is not always complete.

Schwarzenbach[40,41] suggested that the entropy contribution is independent of the nature of the metal ion and of the binding ligand and found that the smallest free energy gain occurs on formation of small chelate rings—a five-membered ring for a saturated bidentate ligand and a six-membered ring for an unsaturated ligand. Hawkins[11] pointed out that elementary calculation of the entropy is possible within the framework of the simple model of a one-dimensional harmonic oscillator by the formula

$$S_\xi = \Delta E/T\,[\exp(-\Delta E/RT) - 1] - R\ln[1 - \exp(-\Delta E/RT)]\ ; \quad (4)$$

where $\Delta E = (2\pi c)^{-1}(K_\xi/\mu)^{1/2}$ is the spacing of the vibrational levels, K_ξ the force constant, μ the effective mass of the oscillator, and c the velocity of light.

A much more effective calculation of the entropy of chelate complexes has been carried out by De Hayes and Busch[20], who also used the harmonic approximation but took into account the entire set of interacting oscillators, having first estimated the frequencies and modes of the normal vibrations of the complex. [We may note that the above workers[20] did not calculate the entropy of the isolated ligands, because they were interested in the contributions of the entropy factor only to the relative stabilities of different spatial isomers of cobalt(III) complexes and not to the stabilities of the complexes themselves]. In the approximation adopted, the following relation is valid for the vibrational entropy of an N-atomic complex:

$$S_{vibr} = R\sum_{i=1}^{3N-6}\{(h\nu_i/kT)/[\exp(h\nu_i/kT) - 1] - \ln[1 - \exp(-h\nu_i/kT)]\}\ , \quad (5)$$

where ν_i are the frequencies of the normal vibrations, h is the Planck constant, and kT the Boltzmann factor.

The translational and rotational entropies can be readily calculated from the formulae[42]

$$S_t = R\left[\frac{3}{2}\ln M + \frac{5}{2}\ln T - \ln p - 3.664 + {}^5/_2\right], \quad (6)$$

$$S_{rot} = R\ln[8\pi^2(8\pi^2 ABC)^{1/2}(kT)^{3/2}/\sigma h^3] + {}^3/_2 R, \quad (7)$$

where M is the molecular weight, p the pressure, ABC the product of the moments of inertia, and σ the rotational symmetry number.

Eqns.(6) and (7) do not give rise to any uncertainties because with their aid the translational and rotational entropies can be calculated exactly. However, we believe that the use of Eqn.(5) is not entirely justified, since, firstly, the configuration entropy can differ very markedly from the vibrational entropy (for example, when there are several minima on the potential energy surface) and, secondly, the vibrations may be significantly anharmonic (the form of the potential well may be far from parabolic). The attempts at a more exact calculation of the contribution of configuration entropy to ΔF_3 are therefore of interest.

It is useful to employ for the estimation of the configuration entropy of the ligands the procedures which had been used previously in the conformational analysis of dipeptides and regular polypeptides[43,45]. We shall assume that the potential energy surface of the ligand is two-dimensional and that it can be represented by a conformational map. For the configuration integral, we can then write

$$Z = \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\exp(-U/RT)\,d\varphi_1 d\varphi_2, \quad (8)$$

where ϕ_1 and ϕ_2 are the angles of rotation, U is the conformational energy, which is a function of these angles, R the gas constant, and T the temperature.

Having at one's disposal a procedure for the calculation of the configuration integral Z, it is possible to determine the free energy:

$$F = -RT\ln Z \quad (9)$$

(we may note that, when the configuration integral is used, no account is taken of the contribution of the kinetic energy to the free energy of the system[45,46], although to a first approximation this contribution can be neglected), the average energy

$$\langle U\rangle = Z^{-1}\int_0^{2\pi}\int_0^{2\pi} U\exp(-U/RT)\,d\varphi_1 d\varphi_2, \quad (10)$$

and the entropy

$$S = \langle U\rangle/T - R\ln Z. \quad (11)$$

Practical calculations can be carried out by replacing integration by summation over a grid. For example, we have for the free energy

$$F = -RT\ln\sum_{\varphi_1}\sum_{\varphi_2}\exp[-U(\varphi_1,\varphi_2)/RT]\,s_0, \quad (12)$$

where s_0 is the area of the elementary square ($\Delta\phi_1$, $\Delta\phi_2$). Clearly the denser the grid of the values of ϕ_1 and ϕ_2, the greater the accuracy of the calculation of the thermodynamic functions. A completely adequate accuracy is as a rule attained using intervals of 5–10° in ϕ_1 and ϕ_2 (summation outside the limits of 20 kJ mol^{-1} contours is pointless, since the contribution of such energetically unfavourable conformers to F is extremely small).

Eqns.(8)–(12) do not take into account the influence of other degrees of freedom—valence angles and bonds. However, this influence is insignificant, since the main contribution to the configuration integral comes from the torsional degrees of freedom (in exactly the same way as the low-frequency vibrations determine almost completely the vibrational partition function).

The situation is more complex when the potential surface of the ligand (or the complex) is significantly multidimensional. In this case the calculation of a multidimensional integral of type (8) is best performed by the Monte Carlo method using one of the variants of the existing selection[47]. On the other hand, if the treatment is restricted to the harmonic approximation, equations of type (5) are valid for thermodynamic functions.

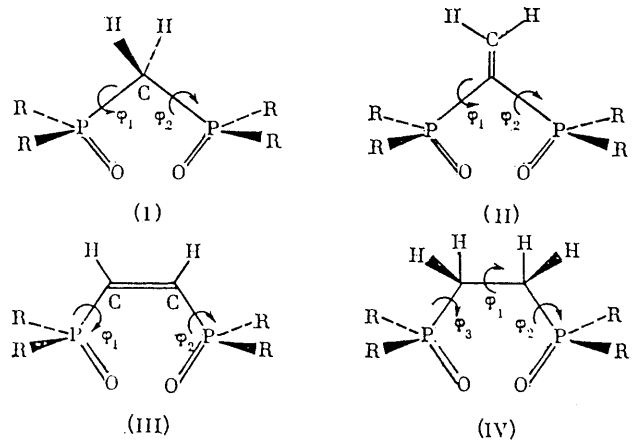


Figure 2. The valence angles and bond lengths in tetramethylmethylenediphosphine (I), tetramethylvinylidenediphosphine (II), tetramethylvinylenediphosphine (III), and tetramethylethylenediphosphine (IV) dioxides. The conformational angles are indicated by curved arrows.

The conformational entropy plays an important role in the determination of the stability of complexes of not only simple bidentate ligands but also complex polydentate ligands. The high complex-forming capacity of macrorings relative to the analogous linear systems is associated with this entropy. Thus the stability of the complex of the cyclic 18-crown-6 polyether with the K^+ ion is ~10^4 times higher than that of the analogous complex of pentaglyme $CH_3O(CH_2CH_2O)_5CH_3$, whose molecule also contains six ligand oxygen atoms[48,49]. This is in fact not surprising because the binding of the pentaglyme molecule to the ion requires the freezing out of several rotational degrees of freedom, whereas in the cyclic system certain degrees of freedom are frozen out (as a result of the ring closure conditions) even before complex formation (in the general case of an asymmetric ring the number of degrees of freedom frozen out, subject to the condition that the valence bonds and angles are fixed, is exactly six; it has been shown[50] that allowance for the ring symmetry decreases this number).

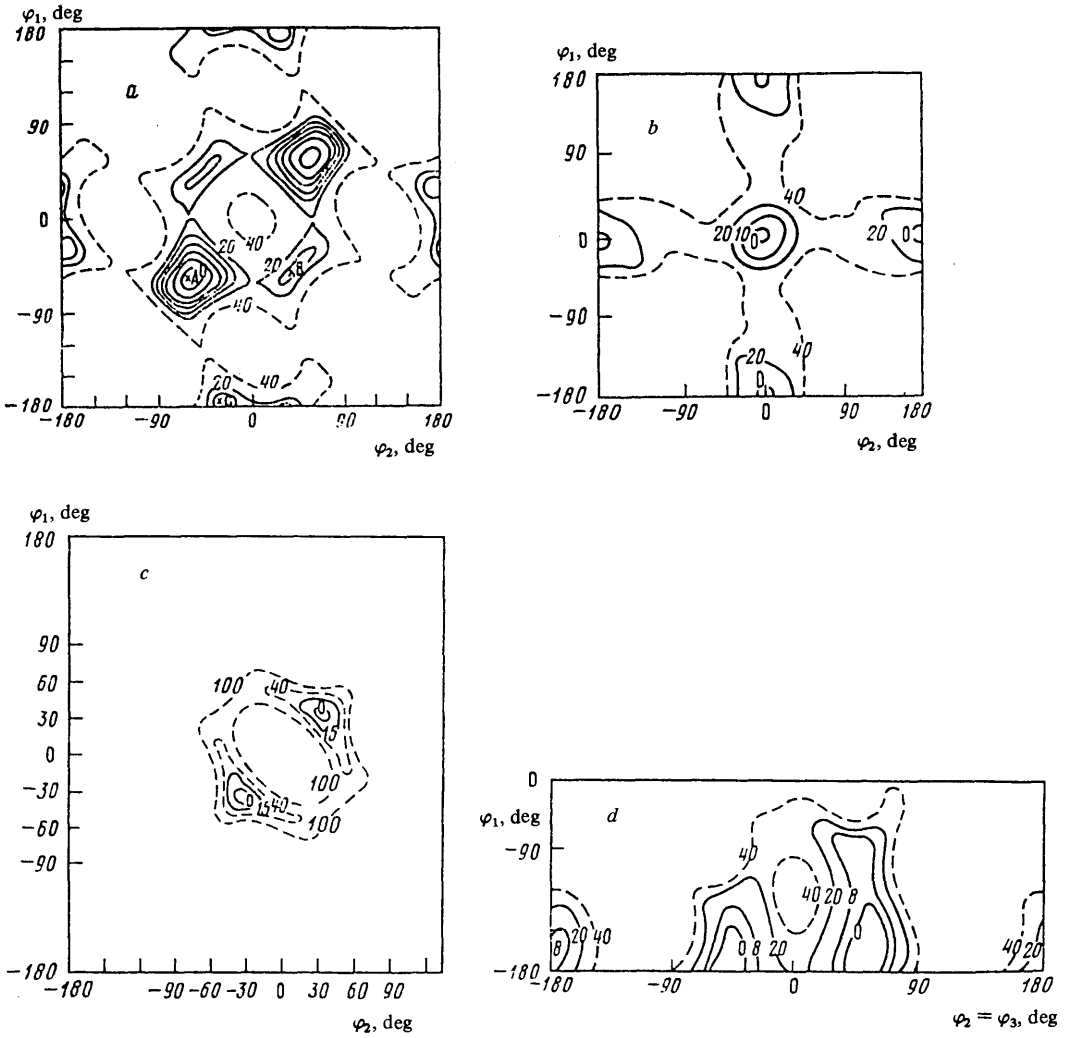


Figure 3. Maps of the conformational energies of ligands (I)–(IV) (*a*–*d* respectively) as a function of the angles of rotation ϕ_1 and ϕ_2. The numerals represent the energies in kJ mol^{-1}.

III. THEORETICAL CONFORMATIONAL ANALYSIS OF THE LIGANDS

1. Chelating Ligands

The considerations described in the previous Section show that the conformational analysis of the isolated ligands permits an approach to the estimation of the selectivity of the complex formation. In fact, if the regions of the conformational map of a rigid ligand corresponding to the required distance $R_{L\ldots L}$ are prohibited, then complex formation is impossible. Furthermore, if the ligand is not sufficiently rigid and the complex formation involves the loss of internal degrees of freedom, then the complex cannot be stable. The complexes formed by rigid ligands subject to the condition that the distance $R_{L\ldots L}$ corresponds to the energy minimum (it is best when this is a global minimum) of the isolated ligand are the most stable.

Taking into account the foregoing, we shall consider the conformational analysis and the estimation of the complex-forming capacities of several *cis*-diphosphine dioxides[51]— compounds which are believed to be highly selective extractants (the methods of synthesis of compounds of this series as well as the procedures used to study some of their properties have been described[52–55]). Although the most complete experimental data are available for the complex formation reactions of phosphine dioxides with various transition metals (many investigators[56–58] pointed out the major role of steric effects), we shall consider their interactions with alkali metal cations, which are characterised by large changes in the crystal-chemical ionic radii and hence in the steric requirements. Fig. 2 presents ligands whose conformations have been calculated within the framework of the model of atom–atom potential function[51,59]. Their choice is not fortuitous because, other conditions being equal, they contain alkylene bridges having different lengths and mobilities and connecting two functional groups. The

geometry of the molecules of compounds (I), (II), and (III) is determined by the internal rotation about the P–C bonds and only in the molecule of compound (IV) is there a possibility of additional rotation about the C–C bond.

Fig.3 presents the conformational maps of ligands (I)–(III) (*a*–*c*) plotted as a function of the angles of rotation ϕ_1 and ϕ_2 for fixed bond lengths and valence angles and also the cross-section of the potential surface of ligand (IV) at $\phi_1 = \phi_3$ (*d*). Fig.3*a* shows that there are three non-equivalent minima on the potential surface of ligand (I) corresponding to forms A, B and C (the first two of these have the C_2 and C_S symmetries respectively). Form A corresponds to the global energy minimum and form B represents an energy loss relative to the former of 15 kJ mol^{-1}. Form C has the open-chain (transoid) structure and is incapable of forming a chelate ring.

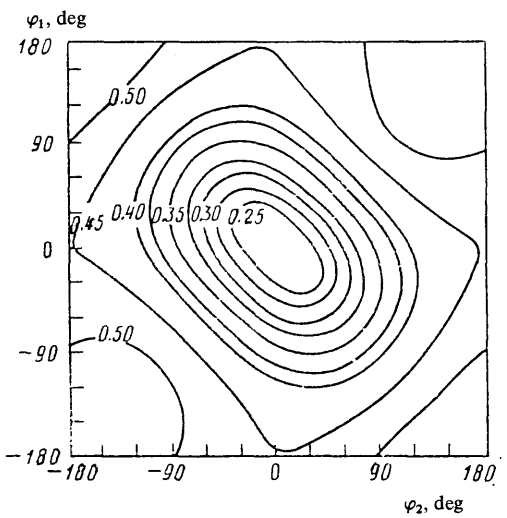


Figure 4. Dependence of the distance $R_{O...O}$ in tetramethylmethylenediphosphine dioxide on the angles of rotation ϕ_1 and ϕ_2 ("distances map"). The numerals opposite the isolines denote the distance in nm.[51]

In order to investigate the possibility of chelation, it is necessary to analyse the possible distances between the donor atoms of the ligand in order to reach conclusions on the basis of the scheme in Fig.1 concerning a suitable radius of the cation. The "distances map" of ligand (I) as a function of the same angles of rotation ϕ_1 and ϕ_2 is presented in Fig.4. If it is superimposed on the conformational map in Fig.3*a*, one can discover immediately which O...O distances correspond to regions with a low energy. It is found that in conformation A the functional groups rotate in such a way that the oxygen atoms are separated by a distance of ~0.45 nm, while in conformation B they approach one another to $R_{O...O} \cong 0.3$ nm. If we now estimate the radii of the alkali metal cations by Eqn.(3) (on the assumption that θ can vary from 75° to 95° and $R_O = 0.15$ nm), we obtain $R_M = 0.12–0.18$ nm and $R_M = 0.05–0.12$ nm for conformations A and B respectively. Thus ligand (I) can form chelate rings with all alkali metal cations and in the complex with Li^+ and Na^+ it must be in the B conformation, while in the complex with K^+, Rb^+, and Cs^+ it must be in the A conformation.

The considerations described show that ligand (I) does not exhibit a high selectivity. However, this does not imply that the constants for its binding to all the cations must be the same or similar. Firstly, there exist "natural" stability series which are independent of the steric factor. Thus it is believed[3] that, in terms of the strength of binding to specific ligands, the cations of alkali and alkaline earth metals as well as the elements of the first transition period can be arranged in the series $Li^+ > Na^+ \geq K^+ > Rb^+ > Cs^+$, $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, and $Zn^{2+} > Cu^{2+} > Ni^{2+} \cong Co^{2+} > Fe^{2+} > Mn^{2+}$. Secondly, the appreciable deformations of the angle θ (up to 75–80° in the complex with Li^+, for example) are energetically unfavourable and lead to a lower stability of the complex. This factor is taken into account in the quasi-elastic model of the solvation shell whereby one can estimate roughly the stability constants of the complexes[6].

We shall now consider the conformational map of ligand (II) (Fig.3*b*). In contrast to the preceding case, here there are deep and narrow potential wells, i.e. the ligand is rigid and hence also selective. One of the minima at the centre of the map corresponds to the cisoid arrangement of the P=O bonds and an O...O distance of 0.28 nm [having carried out the same calculations as for (I), it is easy to show that ligand(II) should bind preferentially to the Li^+ and Na^+ ions]. The other minima are of no interest, since they correspond to the transoid disposition of the P=O bonds which precludes the formation of a chelate ring. We may note that the selectivity of ligand (II) can be significantly increased if the hydrogen atoms of the olefinic group are replaced by bulky groups or halogen atoms. The minimum at the centre of the map then begins to resemble a deep well and the rotations of the phosphoryl groups about the equilibrium positions are extremely limited.

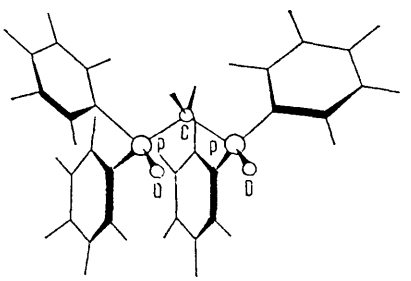


Figure 5. The optimum conformation of tetraphenylmethylenediphosphine dioxide with stacking interaction between the benzene rings[59].

The map in Fig.3*c* shows that ligand (III) must be more selective than (I). It is significant that for this ligand only one conformation, with the C_2 symmetry, is stable while the conformation with a symmetry plane becomes unfavourable owing to the mutual approach of the oxygen atoms. As regards ligand (IV), its conformational map (Fig.3*d*) is very "free" and the ligand cannot therefore be selective. Furthermore, one should bear in mind that the formation of the chelate ring with participation of ligand (IV) must involve the freezing out of three degrees of freedom, which is clearly unfavourable from the standpoint of entropy. Therefore, if ligand (IV) binds an alkali metal cation, only one phosphoryl group is most likely to be involved in such binding.

The conformational calculations described show that, in terms of their selectivities, ligands (I)–(IV) can be arranged in the sequence (II*) > (III) > (II) > (I) > (IV), where (II*) is a halogeno-derivative of (II). Furthermore, having analysed the positions of the energy minima and the $R_{O...O}$ distances maps, one can indicate to which cations particular ligands can be bound.

Analogous conclusions can be reached also for diphosphine dioxides of types (I)–(IV) in which the substituents in the phosphoryl group are phenyl rings and not CH_3 groups[60]. The effective volume of the phenyl rings is not only not greater but actually somewhat smaller than the volume of the CH_3 groups, since they can become readily "adjusted" to the conformation of the main chain as a result of rotations about the P–C bonds. The conformational maps of the phenyl derivatives of compounds (I)–(IV) therefore differ little from the maps discussed above. The difference consists only in the fact that the energy minima are as a rule broader and the barriers are not quite so high. It has been noted[54, 61] that the phenyl-substituted compound with a methylene bridge [compound (I)] forms much more stable complexes with certain cations than the corresponding alkyl-substituted complexes and exhibits an enhanced extractability. Calculation showed that the reason for this "anomalous" behaviour of the compounds consist in the increased stability of the conformations with parallel benzene rings (Fig.5). Such conformation is stabilised by the dispersion interaction of the rings, to which corresponds an energy of ~5–10 kJ mol^{-1} (in the gas phase). The solvent, particularly if it is non-polar, naturally can decrease significantly the above quantity, because the interaction of the benzene rings with solvent molecules can compete with the stacking interaction between the rings; furthermore, a rigid conformation is entropically more favourable than the "mixed" conformation because it causes a lower degree of "structure formation" in the solvent. Nevertheless, in many instances the conformation with parallel benzene rings (the average distance between which is 0.34 nm) is preferred.

We shall now turn to experimental data for the stability constants of the complexes of phenyl-substituted ligands (I)–(IV) with alkali metal cations[62]. These data refer to ethanol–chloroform mixtures with equal proportions of the two components and, strictly speaking, correspond to the equilibrium constants K_{MA}^{ML}, where MA is the metal acetate, and not to K_{M}^{ML}. However, the latter factor is insignificant because the free energy of formation of compounds of type MA from the metal and acetate has been shown by measurements to be the same in all cases and the values of K_{MA}^{ML} presented below therefore differ from the relevant K_{M}^{ML} by the same constant amount. The stability constants of complexes of ligands (I)–(IV) with alkali metal ions are listed below:

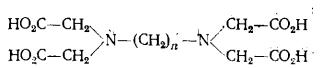
Ion	Li^+	Na^+	K^+	Cs^+
(I)	56	42	20	12
(II)	400	300	—	—
(III)	400	100	40	25
(IV)	10	8	6	7

It is easily seen that the variation of selectivity in the sequence (I)–(IV) deduced by conformational calculations agrees with the experimental trend. Ligand (II), which forms stable complexes with cations of small radius and does not form complexes with large cations, exhibits the greatest selectivity. The least stable complexes are formed, in full agreement with calculated data, by ligand (IV) and it has been established experimentally that only one phosphoryl group participates in complex formation.

Naturally geometrical analysis permits only a qualitative estimation of the relative stabilities of complexes of a series of ligands and cations. In order to obtain quantitative estimates, it is necessary to resort to additional models. In particular, if certain assumptions are made concerning the contributions ΔF_i to the free energy of formation, it is assumed that the energy of deformation of the angle θ (Fig.1) is described by Hooke's law and, after adding together the Boltzmann exponential functions, calculations of the entropy change are made on the basis of conformational maps [see Eqns.(11) and (12)], it is possible to achieve a reasonable agreement between the calculated and experimental stability constants of the complexes[6].

The same principles of the analysis of the steric structure are apparently applicable to hundreds of other ligands synthesised, which are of completely different types, ranging from bidentate to hexadentate, and whose donor atoms may be not only oxygen but also nitrogen, sulphur, phosphorus, and arsenic (we deliberately do not consider in this review complexes containing carbon–metal π- and σ-bonds, because their formation is determined primarily by electronic effects which are usually treated on the basis of the molecular orbital theory). The experimental studies in this field have reached the state where it is possible to speak of the "construction" of ligands which are bound to specific metal ions (this has been specially emphasised in an excellent review[63]) and the task of conformational analysis should be to predict the structures of the ligands.

Conformational analysis, which makes it possible to estimate not only the internal energy but also the entropy of complex formation, can explain the decrease of the stability constants of metal complexes of tetracarboxylic acids of the type



when n varies from 2 to 5 (Schwarzenbach[40]) (the entropy factor associated with the freezing out of certain degrees of freedom on formation of the complex is of primary importance here), and can also account for the topological structure[63] of polydentate chelating agents, the detailed geometry and stability of their complexes with metals, and a whole series of other facts known in coordination chemistry. Since the theory lags far behind the requirements of the experiment in this instance, the sharp increase of the number of theoretical investigations in this field and the appearance of new ideas are to be expected in the foreseeable future.

2. Macrocyclic Complexones

Among macrocyclic complexones the following have become best known: (1) tetradentate chelating agents with strong conjugation throughout the ring and an exceptionally rigid structure in the free state (porphyrins, phthalocyanines, vitamin B_{12}, corrins, and as well as their derivatives and analogues); (2) membrano-active complexones of the peptide and pepsipeptide nature, whose important characteristic is a change in the conformation of the ligand when it is bound to the metal; (3) cyclic polyethers.

The selectivity of the rigid complexones of the first class is actually determined solely by the size of the cavity within the macroring[64]. As regards the relative stabilities of the complexes of a series of ligands with different substituents,

the latter are determined by electronic factors, since the substituents exert a strong influence on the conjugation in the ring.

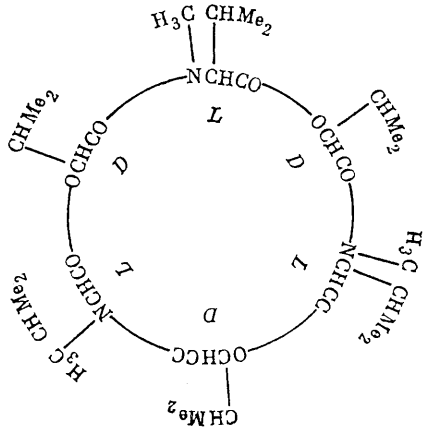


Figure 6. The structural formula of enniatin B.

Among compounds of the second class, there are membrano-active depsipeptide antibiotics such as valinomycin, enniatins, nonactin, antamanide, etc.[65]. The stability constants of the 1 : 1 complexes of three natural macrorings with the Na^+ and K^+ cations (in solution in ethanol) presented below show that the ligands exhibit an appreciable selectivity: two of these bind preferentially to the K^+ ions and one (antamanide) binds preferentially to Na^+ ions. Valinomycin exhibits a unique K/Na selectivity: in its presence the ratio of the K^+ and Na^+ fluxes through mitochondrial membranes is 10000 : 1:

Macroring	Enniatin B	Antamanide	Valinomycin
Na^+	1300	2800	50
K^+	3700	220	$26 \cdot 10^5$
References	[126–129]	[126, 130, 131]	[126, 129]

We shall consider the conformational analysis of the above compounds, which explains their high selectivity. It has been established experimentally that the molecule of enniatin B can assume two conformations depending on the polarity of the medium—the "non-polar" N and "polar" P conformations. Calculations of the conformations within the framework of the model of atom–atom potential functions[66] unambiguously predict these two structures and explain the extensive experimental data on enniatin B (infrared and Raman spectra, etc.).

The fragments of *N*-acetyl-*N*-methyl-L-valine and the dimethylamide of *O*-acetyl-*D*-hydroxyisovaleric acid, whose conformations are described by the angles of rotation ϕ and ψ about the $N-C^{\alpha}$ and $C^{\alpha}-C'$ bonds respectively, can be isolated as the structural units in the enniatin B molecule (Fig.6). Assuming that the ring has the C_{3v} symmetry and that the combination of two pairs of angles ϕ and ψ should lead to cyclic structures, it is possible to find two conformers corresponding to the energy minimum for the entire molecule: the conformer N, in which all the ester and carbonyl oxygen atoms are directed into the interior of the ring, and the conformer P in which they are all directed "outwards". Analysis of spatial models shows that the N conformer can readily bind to the K^+ ion and that a distorted octahedron made up of donor oxygen atoms is formed on the sphere of the central ion. The cavity in the N conformer is too large for the Na^+ ion, which leads to serious deformations of the macroring on binding. On the other hand, if the ions are too large compared with the cavity (Rb^+ or Cs^+), then it has been shown experimentally[65] (p.155) that sandwich structures with the 2 : 1 composition as well as 3 : 1 complexes are the most favourable.

Valinomycin is a 12-membered depsipeptide ring with 36 bonds in the main chain and an alternation of configurations of the type LLDDLLDD... There are in all 24 angles of rotation ϕ and ψ in valinomycin and it would seem, on the ground of general considerations, that less stable complexes are to be expected for this compound than for enniatin B. However, the stability constants quoted above show that this is by no means the case. The question arises of the reason for the anomalously high stability of valinomycin complexes with large cations.

An answer is provided to this question by the results of conformational calculations and the experimental data for both free valinomycin and its complexes. The search for stable conformations of valinomycin without any limitations is naturally associated with serious computational difficulties, because the potential surface has numerous extrema and simple sorting through the possible zeroth approximations would require far too long a machine computation time. Mayers and Urry[67], who carried out calculations within the framework of the model of atom–atom potential functions, therefore used the available experimental infrared and ultraviolet spectroscopic, NMR, optical rotary dispersion, and circular dichroism data for valinomycin and its complexes. They showed that valinomycin has an extremely limited set of low-energy conformations and that in non-polar solvents the "bracelet" form, stabilised by six intramolecular hydrogen bonds, is most favoured. In this form all the oxygen atoms which could, in principle, participate in complex formation are turned "outwards". Another form, also stabilised by siz hydrogen bonds but with the oxygen atoms directed "inwards" into the cavity, is less favourable according to the theoretical calculation (by 250 kJ mol^{-1}). All the remaining conformations correspond to the much more [part of Russian text missing (Ed.of Translation)].

The values presented are naturally too high because the authors[67] did not minimise the potential energy with respect to independent geometrical parameters. In fact, if the other forms possessed such a high energy, they could not have been detected experimentally. Furthermore, spectroscopic data demonstrate the existence of a whole series of forms of valinomycin stabilised by only three hydrogen bonds and also forms in which three oxygen atoms are directed "outwards" and three are directed "inwards", etc. (For a detailed discussion of the conformations of valinomycin and its analogues, see the monograph of Ovchinnikov et al.[65], pp.127–151).

Thus the exceptionally high stability of the complexes of valinomycin with large cations is apparently due to the conformational rigidity of the ligand. Despite the much smaller size of the enniatin B ring, the conformational freedom of its isolated molecule is much greater and its complexes are less stable owing to the decrease of the entropy of the system on complex formation. The selectivity of valinomycin as a complexone is determined by the consumption of the energy required for a deformation of the macroring which ensures a size of the cavity suitable for the given cation. Mayers and Urry[67] calculated the conformational energy of valinomycin as a function of the oxygen–metal distance and showed that the optimum binding should occur for K^+. Binding to a large cation (for example,

Cs^+) requires appreciable opening of the macroring, which entails an increase of the conformational energy. It is not therefore surprising that the stability constant of the valinomycin complex of Cs^+ (in solution in ethanol) is only 6.5×10^5 (compared with 2.6×10^6 for the complex with K^+).

Calculations of the geometry and energetics of certain other natural macrorings have been carried out at a higher level than in the study of Mayers and Urry[67]. The conformational calculation for nonactin[68], whose molecules selectively transfer K^+ ions through phospholipid layers and which contain 32 bonds in the main chain, is instructive. The first stage of the calculation consisted in the selection of the allowed regions of the conformational space by the hard sphere method. It was assumed that the molecule has the same symmetry S_4 as the corresponding chemical formula. Next the potential function was scanned with respect to five symmetrically independent conformational angles; for this purpose, 2×10^6 conformations, i.e. $(360/20)^5$, were examined overall, since the scanning for each angle was carried out at 20° intervals. After the minimisation of the potential function, only 7 conformations had energies within the limits of 21 kJ mol^{-1} and 39 had energies within the limits of 42 kJ mol^{-1} (if the energy of the global minimum is adopted as the zero point). It is noteworthy that all the energetically favourable conformers constitute a single family, i.e. they occupy a fairly narrow region of conformational space. The shape of the molecule then resembles a tennis ball in which there is an aperture compatible with the size of the K^+ ion. The detailed geometry of nonactin and its complex with K^+, found by Lee and Hamori[68], agrees extremely well with the results of X-ray diffraction analysis.

Another approach has been used to investigate the conformations of antamanide[69]—a macroring of approximately the same size as nonactin. Initially the antamanide molecule was subdivided[69] into fragments and low-energy conformers of the latter were selected, rejecting those which are clearly unfavourable; after this, the complete calculation was carried out taking into account all the degrees of freedom.

Synthetic polyethers of the type $(-CH_2-CH_2-O)_n$, for whose complexes with alkali metal cations numerous experimental stability constants, steric structures of the molecules, etc. are available [see, for example, Ovchinnikov et al.[65] (pp.64–78) and Refs.193–204], give rise to an interesting class of macrocyclic complexes. Theoretical studies of the conformations of these compounds and of the selectivity of their complex formation reactions so far lag behind the experimental investigations and our knowledge is limited to estimates of the dimensions of the cavities (carried out[48,70,71] by studying spatial models) and some quantum-chemical calculations[72–78]. The diameters of alkali metal cations are compared below with the dimensions of the cavity in the macroring D (the lowest value corresponds to the Corey–Pauling–Coltun model and the highest to the Fisher–Hirschfelder–Taylor model):

Cation	Li^+	Na^+	K^+	Cs^+
d, nm	0.136	0.194	0.266	0.334
Macroring	12-crown-4	15-crown-5	18-crown-6	21-crown-7
D, nm	0.12–0.15	0.17–0.22	0.26–0.32	0.34–0.43

(in the trivial names of the compounds the first numeral corresponds to the number of bonds in the macroring and the second to the number of oxygen atoms). On the basis of the data presented, the molecule of 12-crown-4 should bind more strongly to the Na^+ cation than to K^+; the following stability series should hold for the different polyethers: $Na^+ \cong K^+ > Cs^+$ for the 15-crown-5 polyether; $K^+ > Cs^+ > Na^+$ for the 18-crown-6 polyether; $Cs^+ > K^+$ for the 21-crown-7 polyether. These predictions are satisfactorily correlated with the experimental data for the stabilities of the complexes in solutions. However, in many instances certain deviations are observed, associated with the formation of sandwich structures (if the cation cannot be accommodated in the cavity, it is "clamped" between two macrorings, which results in a 2:1 "sandwich").

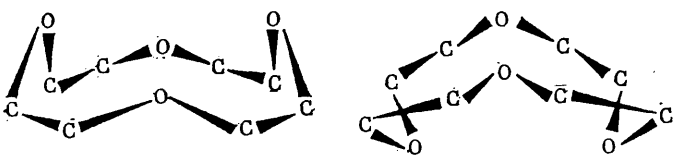


Figure 7. Schematic representation of the maxidentate (*a*) and alternate (*b*) conformations of the 12-crown-4 polyether.

We shall now consider quantum-chemical calculations of the conformations and on the energetics of the complex formation reactions of the crown ethers[72]. The conformational energies of the molecule of 12-crown-4 and the potential surfaces of the interaction of this molecule with the Li^+ ion have been calculated by the non-empirical self-consistent field LCAO-MO method in terms of the STO-3G basis. For an isolated molecule, the calculation was performed on the assumption that the C_4 symmetry (form M, maxidentate) or C_2 symmetry (form A, alternate) is retained with the standard bond lengths and valence angles (Fig.7). Subject to the limitations indicated, the only independent parameter determining the conformation of the macroring is the angle of rotation about the O–C bond χ; the remaining angles of rotation can be calculated from the symmetry and ring closure conditions.

The calculations made it possible to find the optimum value of χ for each conformer and showed that form A is more stable than form M (the energy of form A is lower by 16 kJ mol^{-1}). However, as a result of the interaction with the Li^+ ion, the maxidentate form is naturally preferable; here the equilibrium value of the angle χ in the Li^+ complex becomes different and depends on the distance d between the Li^+ ion and the centre of the molecule. Fig.8, which presents the dependence of the total energy of the system on the angle χ for three values of d, shows that the "expulsion" of the Li^+ ion to a certain distance from the plane of the macroring constitutes the optimum configuration and is apparently best when $d = 0.04$ nm. This factor as well as the deformation of the macroring on its interaction with the ion was not taken into account by Pedersen and Frensdorff[71] in their explanation of the selectivity of macrocyclic polyethers which they based on the analysis of spatial models. Nevertheless it can play a major role in complex formation (this is indicated also by data for the structure of the crystalline complex of 18-crown-6 with the Na^+ ion obtained by X-ray diffraction[79]).

It is noteworthy that the relative stabilities of the different conformers of macrocyclic polyethers predicted by calculation depend both on the method of calculation and on the parametrisation. For example, in contrast to the *ab initio* calculation examined, the CNDO/2 method predicts that form M of 12-crown-4 is favourable[76,78] and, according to Guzikevich et al.[78], the difference between energies of

forms A and M for this ether exceeds 100 kJ mol^{-1} (!). However, the CNDO/BW (Boyd–Whitehead) parametrisation leads to the conclusion that the stability of form A is higher[77]. One cannot rule out the possibility that calculations within the framework of the model of atom–atom potential functions will throw light on the problem of the relative stabilities of the conformers of crown ethers.

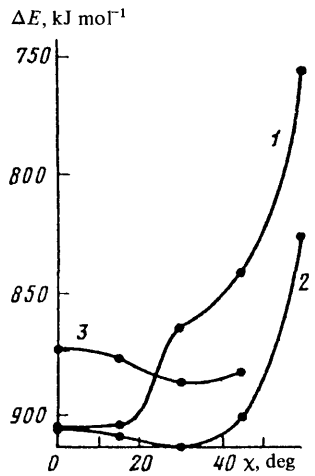


Figure 8. The energy of the interaction ΔE of the Li^+ ion with a molecule of 12-crown-4 in the conformation M as a function of χ for different values of d: *1*) 0; *2*) 0.4; *3*) 0.8.[73]

The examples examined show that both the structure of the spatial models and theoretical calculations of the conformations make it possible to explain the selectivity of natural and synthetic macrocycles with respect to specific alkali metal cations. However, for a quantitative prediction of the stabilities of the complexes, more detailed calculations are needed which take account not only of ΔE_3 corresponding to the change in the potential energy of the ligand, but also of the entropy of complex formation and of the influence of the solvent#.

IV. INTERLIGAND INTERACTIONS AND THE STERIC STRUCTURE OF COORDINATION COMPOUNDS

The steric structure of coordination compounds containing chelate rings and/or monodentate ligands is to a large extent determined by the interactions between the ligand atoms. Even if one considers simple cation–bidentate ligand complexes, these interactions also occur, because the vertices of the coordination polyhedron are occupied by the donor atoms of the solvent molecules.

The first attempt to analyse the disposition of the donor atoms on the sphere of the central ions was undertaken by Zemann[81], who examined the interaction of five point charges of the same sign on the basis of Coulomb's law.

#For the analysis of certain thermodynamic problems of chelation and macrocyclisation in solution, see Yatsimirskii[80].

Kepert[82–85] developed an approach based on allowing for the mutual repulsion of the donor atoms in the form $U_{ij} = ar_{ij}^{-n}$, where r_{ij} is the distance between atoms i and j, a a constant, and n the power exponent, which can assume values of 1 (Coulomb's law), 12 (repulsive component of the Lennard-Jones potential), or some other intermediate value (for example, 6). The energy of the complex is calculated from the formula $U = \Sigma U_{ij}$.

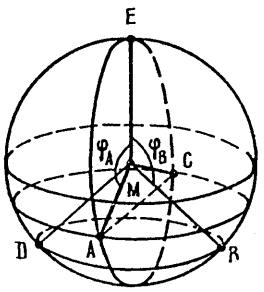


Figure 9. Schematic representation of a complex with five monodentate ligands. The metal cation M is in the centre of the sphere. The planes of the two cross-sections shown under the large circle are parallel by virtue of the pair equivalence of the ligands A, C and B, D.

We shall consider as an example the calculation of the geometry of a pentacoordinate compound with five monodentate ligands. If ligands A and C and also B and D are equivalent in pairs, the stereochemical structure of the complex can be expressed as a function of the two independent angles ϕ_A and ϕ_B (Fig.9). For $\phi_A = \phi_B$, the configuration of a tetragonal pyramid obtains; on the other hand, if $\phi_A = 90°$ and $\phi_B = 120°$ (or conversely), the configuration of a trigonal bipyramid arises.

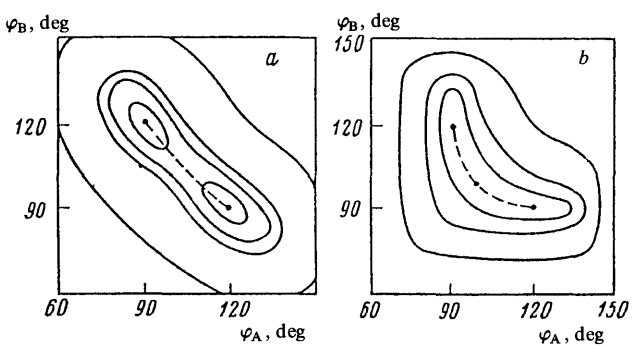


Figure 10. Contours on the potential surface (energies in relative units) of a compound M(monodentate)$_5$: *a*) for $n = 1$ in the formula of the potential $U = \sum_{i>j} \sum a r_{ij}^{-n}$; *b*) for $n = 12$.[87]

Fig.10 presents the potential surface of the coordination compound in terms of the parameters ϕ_A and ϕ_B. It is easily seen that, for $n = 1$ (i.e. when the Coulombic

repulsion of the donor atoms predominates), the trigonal bipyramid is energetically favourable, while the configuration of the tetragonal pyramid corresponds to the saddle point (Fig.10*a*). For $n = 12$ (when the repulsion of the electron shells of the atoms predominates), the last configuration becomes optimal. This calculation permits the conclusion that bulky ligands promote the appearance of the tetragonal pyramid, while ligands with residual charges on the donor atoms promote the trigonal bipyramid. However, Kepert did not reach this conclusion[82-85]. Instead he adopted the value $n = 6$, which ensured the best agreement with numerous and also extremely varied experimental data.

The value $n = 6$ found by Kepert lacks physical significance, since it corresponds to dispersion attraction with, however, the sign reversed. Examination of the interaction potentials of the donor atoms or ligands as a whole in the form of the sum of the terms with r^{-1} and r^{-12} is more realistic: if the coefficient of r^{-1} is much greater than the coefficient of r^{-12}, then Coulombic repulsion predominates; in the opposite case the geometry of the complex is determined mainly by the repulsion of the electron shells. Incidentally, there is altogether no need to employ terms with r^{-12}; the treatment can be based also on Kitaigorodskii's universal atom–atom potential[86], which depends only on the single parameter r_0. Then all calculations of this kind can be usefully performed for different values of the normalised bite of the donor atom r_0/l, (where l is the length of the coordinate bond) and for different charges on the donor atoms. In this case one other theoretical parameter has to be added (because a term of the type ar_{ij}^{-n} "is split" into two terms), but this formulation of the problem makes it possible to understand to what extent the geometry of coordination compounds is determined by electrostatic interactions and to what extent by steric hindrance.

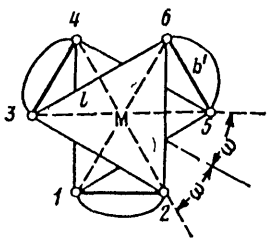


Figure 11. The view of a regular octahedron "from above". It can be represented as a prism whose upper and lower bases are rotated in opposite directions by the angle ω. The numerals denote the numbers of the donor atoms; b' is the distance between the donor atoms of one ligand.

It has been suggested[87] that a generalised dispersion-Coulombic potential, which is the sum of Kitaigorodskii's potential and the energy of the Coulombic interaction of point charges equal in magnitude, be used for the calculation of the relative stabilities of different polyhedra. The interligand interaction energy calculated with the aid of this potential is minimised on the basis of several zeroth approximations corresponding to the proposed steric structure. The possible equilibrium structures, which in the general case can differ from the ideal configuration (prism, octahedron, etc.) and determine the difference between the energies of different configurations, are then found.

The approach described has been applied to the study of the M(monodentate)$_5$, M(monodentate)$_6$, and tris(bidentate)M systems. We shall consider some results obtained[88] for the tris(bidentate)M system, which is represented conventionally in Fig.11 (the metal M is in the centre of a sphere on which the donor atoms of the ligands are distributed). It is easily seen that the configuration of the complex depends on the trigonal distortion angle ω: when $\omega = 30°$, the configuration of a regular octahedron arises and for $\omega = 0°$ that of a trigonal prism is produced; for intermediate values of the angle, the configuration is not highly symmetrical and it is usually classified as a distorted prism (it is assumed that, on distortion of the trigonal prism, both triangles shown in Fig.11 rotate by the angle ω in opposite directions relative to the "ideal" configuration with D_{3h} symmetry).

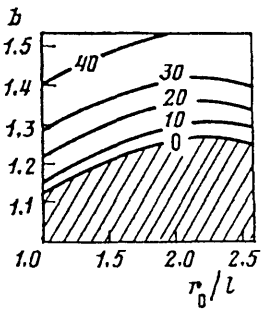


Figure 12. The equilibrium values of the trigonal distortion angle ω for different values of b and r_0/l ($q = 0.4\ e$). The isolines denote the values of the angle in degrees. The shaded regions correspond to the trigonal prism configuration[88].

The equilibrium structure of the complex must evidently be determined by purely geometrical factors (l and b', where b' is the distance between the donor atoms of a single ligand) and also by the potentials of the interaction of donor atoms (in principle, these should be the effective potentials of the interligand interaction). Calculations of the equilibrium structure were carried out for different values of the normalised bite of the ligand $b = b'/l$ and for different charges on the donor atoms ($q = 0.0\ e$, $0.1\ e$, $0.4\ e$, and $1.0\ e$) on the assumption that r_0(O...O) is 0.30 nm. Fig.12 presents a diagram indicating the equilibrium value of the trigonal distortion angle ω for different values of b and r_0/l and for $q = 0.4\ e$ (analogous diagrams were also constructed for other charges). The trigonal prism configuration corresponds to the shaded region. On the other hand, a considerable proportion of the diagram corresponds to distorted configurations—intermediate between the prism and the octahedron, a comparatively small region corresponding to the ideal octahedron ($\omega = 30°$) [in contrast to compounds of the type M(monodentate)$_6$ for which the octahedral configuration is preferred for all values of r_0/l except very low ones]. Analysis of various diagrams of this kind shows that, with increase of the charge q, the region of the stability of the trigonal prism diminishes.

On the basis of the data in Fig.12 (for $q = 0.4\ e$), we shall examine the results of the calculation of the trigonal distortion angle ω in relation to several fairly arbitrarily selected compounds (see Table). The Table shows that, despite a whole series of assumptions made in the model (for example, the assumption that all the donor atoms are distributed on

the sphere of the central ion), the agreement between the calculation and experiment is entirely satisfactory and not only for alkali and alkaline earth metal cations, whose binding is ionic, but also for transition metals, for which preferred directions of binding are frequently postulated. The points on a sphere model arises from the idea that in the ion itself there are no preferred directions and that, when they arise, this is solely due to the interaction of the ligands and their donor atoms. Whether or not this model conflicts with quantum-chemical results should be revealed by future investigations.

Parameters of the complexes.

Compound	Polyhedron	l, nm	r_0, nm	r_0/l	b, nm	ω, deg	
						calc.	expt.
$Cu\{[Me_2N]_2P(O)OP(O)\{NMe_2\}_2\}_3(ClO_4)_2CuO_6$	CuO_6	0.207	0.30	1.45	0.139	32	38
$Mg\{[Me_2N]_2P(O)OP(O)[NMe_2]_2\}_3(ClO_4)_2$	MgO_6	0.206	0.30	1.46	0.136	30	36
$Na[Ph_2P(O)CH_2P(O)Ph_2]_3I$	NaO_6	0.245	0.30	1.22	0,115	0	0
$Mn[MeC(O)CHC(O)Me]_3$	MnO_6	0.200	0.30	1.50	0.140	33	38
$V[MeC(O)CHC(O)Me]_3$	VO_6	0.198	0.30	1.51	0.139	32	37
$[Cu(NH_2CH_2CH_2NH_2)_3]SO_4$	CuN_6	0,215	0.32	1.49	0.130	24	24
$[Co(NH_2CH_2CH_2NH_2)_3]SO_4$	CoN_6	0.200	0.32	1.60	0.140	31	30
$[Ph_4As]_2[W(CNC(S)C(S)CN)]$	WS_6	0.237	0.39	1.64	0.131	18	14
$(Me_4N)_2[Fe(CNC(S)C(S)CN)]$	FeS_6	0.226	0,39	1.72	0.139	29	36

V. CONFORMATIONAL ANALYSIS OF CHELATE RINGS AND COMPLEXES

Calculations of the conformations of isolated ligands, whereby conclusions concerning the selectivity of the complex formation can be reached, were considered in Section III. Here we shall deal with analogous calculations for ligands bound to the metal cation by coordinate bonds. For classical ethylenediamine complexes (the $H_2NCH_2CH_2NH_2$ ligand), in which the chelate rings contain five bonds (of these two are coordinate bonds), conformational studies within the framework of the model of atom–atom potential functions were carried out by Gollogly and Hawkins[16–18,89,90]. The ideal angle θ (Fig.1) was assumed to be 90° and its deformation was described by the harmonic law with the elastic constant determined from spectroscopic data. As a result, it was shown that the five-membered ring can have two stable conformations (half-chair and envelope) and that whether or not a particular form is favourable is dictated by geometrical limitations: if the metal–donor atom bond length is less than 0.175 nm, the envelope form is preferred; for longer bonds, the half-chair form is usually realised.

The problem of the relative stabilities of the five- and six-membered chelate rings has been recently investigated[91,92], the authors having calculated the conformations of nickel(II) complexes with eight different ligands within the framework of the method of atom–atom potential functions. Among the ligands, ethylenediamine and diethylenetetramine could form five-membered rings, while 1,3-propylenediamine and dipropylenetriamine could give rise to the corresponding six-membered rings. It was found that the experimentally observed reduced stability of the six-membered rings may be fully attributed to steric strain and that the main contribution to the difference between the enthalpies of the five- and six-membered rings comes from the deformation of the valence angles and non-valence interactions.

Depending on the position of the substituent at the asymmetric carbon atom, *C*-substituted ethylenediamines can have two configurations—*R* and *S*. For each structural isomer, there is equilibrium between the λ- and δ-conformers (as shown for 1,2-diaminopropane in the *R*-configuration), in one of which (λ) the methyl group occupies the equatorial position and in the other (δ) the axial position. These conformers can be interconverted after overcoming a potential barrier whose magnitude is ~40 kJ mol^{-1} according to the measurements of the temperature dependence of the ^{13}C NMR spectra of complexes of diamines with cobalt, molybdenum, and tungsten[93].

However, not only the barrier but also the difference between the energies of the conformers is significant for complex formation. In an early pioneer study, Corey and Bailar[94] found that the λ-conformer is more stable by ~4 kJ mol^{-1}. Calculations by other workers[11], based on the minimisation of the potential energy, showed that this difference should be even smaller. According to estimates[20,21], the difference between the free energies ΔF of the axial and equatorial conformers (δ and λ for the *R*-isomer) depends mostly on the entropy contribution, which the authors[20,21] took into account within the framework of the harmonic approximation for interacting oscillators (see Section I). As a result, they obtained $\Delta F = 10$ kJ mol^{-1} and noted that allowance for the entropy leads in almost all cases to an increase of the free energy difference compared with the value of ΔE calculated by minimising the potential energy. Thus the potential well corresponding to the more "strained" δ-conformer is narrower.

Conformational analysis of the different *C*- and *N*-methyl- and dimethyl-substituted ethylenediamines as well as numerous six-membered chelate rings has been described in detail in a monograph[11]. The chair conformation of six-membered rings is the most stable; the twist-form is less favourable in almost all cases, but the presence of particular substituents can influence the difference between the energies of these forms. The problem of the stability of the axial and equatorial conformers of six-membered rings is in many respects similar to the analogous problem for substituted cyclohexanes and, since it has been thoroughly investigated, we shall not consider it.

However, we believe that the problem of parametrisation requires further study. All the workers who investigated the conformations of chelate rings assumed that the ideal value of α_0 (or the angle θ_0 if the scheme in Fig.1 is resorted to) should be 90°. Furthermore, from both the standpoint of quantum mechanics and general considerations, the presence of any preferred directions of binding at the metal atom appears doubtful. It is most likely that the angle α_0 (or θ_0) is dictated by the conditions of the environment of the metal atom (octahedral or square configuration of the metal cation) and the most direct method of taking into account the environment consists in the complete analysis of the interligand interactions on the basis of the model of atom–atom potentials. There is then no need to make any assumptions about the values of α_0 (θ_0) and the corresponding elastic constant *C*. On the other hand, in calculations on isolated chelate rings, α_0 and the constant *C* take into account implicitly the interaction of the ligand atoms with the solvent molecules, but in this approach *C* may vary on passing from compound to compound and from solvent to solvent.

In classical bistridentate complexes of cobalt(III) with ethylenediamine ligands, their derivatives, and aminoacids, the stabilities of different conformations of the chelate rings are determined in many respects by the interaction between the rings. The combination of λλλ conformations

is therefore not always energetically the most favourable. Calculations of the conformations of such complexes have been analysed in a review[15] (see also later publications[95-101]) and certain improvements to the method of calculation, consisting, in particular, in allowance for the symmetry of the complex and the conformational entropy of the ligands, have been described[102]. As a result of these improvements and also of the more accurate specification of the force field for certain fairly involved complexes, the theoretical structural parameters are almost exactly identical with X-ray diffraction data.

However, one should note that the calculation does not always yield unambiguous information about the most favourable structure. Niketič and Woldbye[24,25], who carried out exceptionally troublesome and laborious computer experiments in order to discover the possible conformers of trisdiamine complexes of cobalt(III) with three six-membered chelate rings and also similar complexes with dimethyl-substituted ligands, concluded that the situations where the potential surface contains several wells of comparable depth are typical. In solution there should therefore be equilibrium between several conformers and in the crystal (by virtue of the influence of intermolecular interactions) the most favourable conformer need not necessarily obtain. The predictions of the theory are fully unambiguous concerning the relative stabilities of the axial and equatorial conformers of different methyl-substituted derivatives and agree with experimental data.

Calculation of the relative stabilities of the conformers of involved complexes is most closely related to the problem of stereoselectivity[103]. Stereoselective reactions are understood to be those which result in the formation of two or several isomers of different chirality and one of these is present in the equilibrium mixture in a greater relative amount than the others, so that it becomes possible to isolate it by means of a series of technical procedures (in contrast to stereospecific reactions which lead to the formation of only one isomer).

The problem of stereoselectivity is too wide to be considered in the present review in any detail. We shall attempt to answer the question whether it is possible to predict theoretically the relative energies of isomeric complexes and to outline the procedures for the most effective stereoselective synthesis. In the first place one should note that the differences between the energies of the chelate rings formed by DD- and LD-ligands, for example, aminoacids, are extremely small, which is shown particularly by the results of calculations carried out by Hawkins[11] (the greatest energy difference is reached for the diastereoisomers of proline). Furthermore, the interaction with the solvent, which is usually disregarded in conformational calculations, plays a major role in determining the stability of the diastereoisomeric complexes. Finally, one must bear in mind that the intermediates formed in the reaction are not true transition states and that their energies can be regarded as proportional to the energies of the transition states only with some approximation.

Hawkins therefore viewed very pessimistically the possibility of a theoretical prediction of stereoselectivity. However, accurate conformational calculations carried out in recent years apparently have disproved this view. We may point out, in particular, studies[104,105] devoted to the conformational analysis of involved isomeric cobalt(III) complexes of glycine and alanine (the predicted[104,105] differences between the energies of the diastereoisomers were ~3–5 kJ mol^{-1}, which corresponded to a 60–80% yield of one of the isomeric forms); a satisfactory agreement with the available experimental data was achieved.

* * *

Summarising, we may note that the method of theoretical conformational analysis makes it possible to interpret and predict, on the basis of calculation of ΔF_3, the relative stabilities of metal complexes and the selectivities of the complex formation and that in many instances it is important to take into account the solvation shell, which can be done both in the continuum model and in an explicit form. In the latter case it is useful to make the calculation gradually more complex by considering in succession the conformations of the chelate ring and the interactions between the solvent molecules and/or the chelate rings. Since this problem involves many extrema when it is formulated in terms of the atom–atom approximation, the optimisation of the positions of the donor atoms on the sphere of the central ion constitutes an important auxiliary stage whereby one can find the possible zeroth approximation and predict the stereochemical configuration of the complex.

However, the calculation need not of course be carried out in this sequence in all cases. For example, the model of interacting points on a sphere has no direct bearing on complexes with macrocyclic ligands. Furthermore, in the general case certain aspects of the selectivity of complex formation can be understood simply on the basis of the conformational analysis of isolated ligands.

Theoretical studies of the stability of metal complexes and of the selectivity of complex formation are only just beginning and it must be supposed that in the near future new interesting results will be obtained in this field.

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Heterometallic Ferrocene-based Transition Metal Compounds

P.N.Gaponik, A.I.Lesnikovich, and Yu.G.Orlik

The literature data on the synthesis, properties, and applications of ferrocene derivatives containing a *d* element or its inorganic and organic derivatives in the molecule are described systematically and surveyed.
The bibliography includes 293 references.

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I. INTRODUCTION

The practical applications of ferrocene and its derivatives have greatly expanded in recent times[1-4] primarily due to the successful development of synthetic studies on this extremely interesting class of compounds.

Among the wide variety of ferrocene derivatives, compounds containing in the molecule another transition metal, namely dinuclear and polynuclear heterometallic derivatives of ferrocene (HMF), occupy a special place. They have been investigated extremely vigorously in recent years. More than 300 compounds have been synthesised and extensive experimental data on their properties and practical applications have accumulated. It is noteworthy that the principal results for HMF have been obtained in the last ten years and as yet have not been adequately surveyed in the literature. The majority of the studies published up to 1970 are discussed in monographs[5-7]. Individual scattered data on HMF have also been published in annual reviews on ferrocene[8-19] and in Gmelin's handbooks[20-25]. A review devoted to ferrocene-containing metal complexes, in which these compounds have been formally classified on the basis of the nature of the heterometal, was published[26] in 1981. It covers up approximately one-third of the published literature but little attention is devoted to the chemistry of HMF, in particular its synthetic aspects.

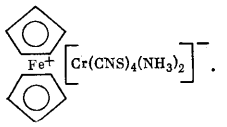
The aim of the present review is to give a systematic account of the literature data, mainly on the synthesis and also on the properties and applications of HMF, and to classify the existing compounds. The generalisations made concerning the methods of synthesis of HMF can be used to develop procedures for the preparation of polynuclear compounds based on other organometallic compounds of transition metals. The literature up to 1980 inclusive and the majority of the publications in 1981 are covered.

II. TYPES OF HETEROMETALLIC DERIVATIVES OF FERROCENE AND METHODS OF THEIR SYNTHESIS

HMF can be most rationally classified taking into account the characteristics of the chemical bond whereby the ferrocene fragment is coupled to a derivative of another metal in the course of the formation of the HMF. This approach takes into account not only the specific features of the bond but also its genesis, reflecting thereby to some extent also the method of synthesis of the compound. The proposed classification of HMF is used in this review and in its subdivision into sections.

1. Salts of the Ferrocenium Cation

One of the most unusual reactions in the chemistry of ferrocene is its oxidation to the ferrocenium cation, which takes place readily in an acid medium[20]. In order to obtain the HMF, the ferrocenium cation may be combined with an anion incorporating the transition metal atom. The first bimetallic salt obtained in this way has been ferrocenium reineckate[20]:



This salt precipitates when an acid solution of ferrocenium sulphate is mixed with a solution of the Reinecke salt. The infrared spectra[27] and thermal decomposition[28] of this compound have been investigated. Ferrocenium molybdate, tungstosilicate[27], metatungstate, and tetravanadate[29,30], which are solid powders insoluble in organic solvents, were obtained similarly to the reineckate. The formula $[FcH]MoO_4$ was attributed[27] to the molybdate†. There is a possibility of the formation of $[FcH]Mo_8O_{26}.2H_2O$, which is associated with the polymerisation of the molybdate ions in an acid medium and the tendency of ferrocenium cations to form precipitates with bulky anions[30]. The reineckates of substituted ferrocenes have also been isolated[21,31].

A series of compounds of the ferrocenium cation with noble metal anions have been obtained: ferrocenium hexachloroplatinate $[FcH]PtCl_6$ [from ferrocenium chloroferrate(III) and chloroplatinic acid][32] and salts with gold-containing anions[33]: $[(FcX)^+(AuCl_4)^-]_3Au$, where X = H, Cl, Br, I, Et, Ph, CN, NO_2, COMe, COPh, or COOMe. These compounds are almost quantitatively precipitated on interaction of ferrocene derivatives with chloroauric acid. In a number of instances (X = H, Cl, CN, COOMe) gold was washed out with aqua regia and the compounds $[FcX]AuCl_4$ were isolated.

Similar complexes of palladium $\{[FcH]PdCl_3\}$,[34] iridium $\{[FcH][IrCl_4(PMe_2Ph)_2]\}$,[35] vanadium $\{[FcH]VOX_3(X = Cl \text{ or } Br)\}$,[36-39] and titanium $\{[FcH]TiCl_4\}$[38,39] were obtained by the reaction of ferrocene with the corresponding salt in a hydrocarbon medium in the absence of oxidants. The ionic nature of the compounds was confirmed by Mössbauer[34], ultraviolet, and infrared spectroscopy[36,37]. Thermochemical

† Here and henceforth Fc = ferrocenyl ($C_5H_5FeC_5H_4$) and correspondingly FcH = ferrocene.

study of the formation of complexes of ferrocene with Lewis acids[38] showed that an ionic complex is formed if the energy of the donor–acceptor bond exceeds the ionisation energy of ferrocene. There exists also information about the synthesis of a ferrocenium salt with a complex nickel-containing anion: $[FcH][Ni(S_2C_4F_6)_2]$.[20] Single crystals of this compound exhibit a high conductivity.

2. Salts of Ferrocene-containing Acids

Compounds of this type are obtained by the reaction of the corresponding acid with transition metal salts. The copper salts of ferrocenecarboxylic[22,40], ferrocenedicarboxylic[5], and ferrocenylcyanoacrylic acids[24], as well as the uranyl salts of ferrocenemonocarboxylic and ferrocenedicarboxylic acids[41] have bee described. Such salts, which are coloured powders insoluble (with some exceptions[42]) in organic solvents, have been described also for other ferrocene acids; ferrocenemonosulphonic acid $[(Fc{-}SO_3)_2M.4H_2O$, M = Cu or Mn], [43] ferrocenedithiocarboxylic acid $[(Fe{-}CSS)_2M$, M = Cu,[40] Co, Ni, Mn, Cu, Pd,[42] or MoO_2 [44]], ferrocenehydroxamic acid $[(Fc{-}CONHO)_2Cu]$, and ferrocenylacetylhydroxamic acid $[(Fc{-}CH_2CONHO)_2Cu]$.[45,46]

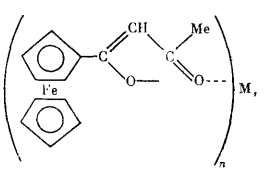
The fairly stable gold-containing derivatives of thioferrocene, which is dimeric in solution and is obtained by the exchange reaction[47]

$$Fc{-}SNa + ClAuPPh_3 \rightarrow Fc{-}SAuPPh_3 ,$$

may be assigned to the same type of HMF. Its interaction with fluoroboric acid results in the formation of the cationic complexes $[Fc{-}S(AuPPh_3)_2]^+BF_4^-$ and $[Fc{-}S(AuPPh_3)_2PPh_3]^+ . BF_4^-$.

3. Chelate Compounds

One of the ways of synthesising HMF involves the use of ferrocene-containing β-diketones as chelating ligands. Stable compounds soluble in organic solvents have been obtained from acetoacetyl ferrocene in 70–90% yield:[22,48–57]



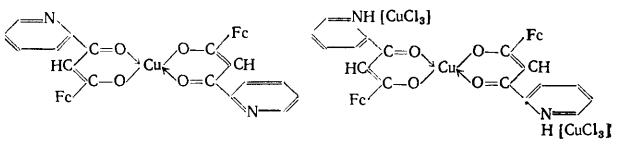
M = Ni, Co, Cu, Mn, Cr, VO, Ru; $n = 2, 3$.

Like metal acetylacetonates, they are capable of forming adducts with electron-donating molecules (pyridine and water)[49–51,56]. Nickel ferrocenoylpivaloylmethanate[58], copper ferrocenoylbenzoylmethanate[53], copper, palladium[53], allylpalladium[59,60], and ruthenium[57] ferrocenoyltrifluoroacetonates, a series of copper[61] and uranyl[41,62] complexes of 1,1′-bis-(acetoacetyl)ferrocene and 1,1′-bis(benzoylacetyl)ferrocene, the ethylenediaminenickel complex of 1,1′-bis(acetoacetyl)-ferrocene[63] and the cyclopentadienylnickel complex of ferrocenoyltrifluoroacetone (NFTA) [64] have also been described. The metal : iron ratio in these compounds varies with the oxidation state of the metal ion and the number of β-diketone substituents in ferrocene. In contrast to its fluorine-free analogue, in reactions with dichlorometallocenes under mild conditions, NFTA substitutes a chlorine atom and a cyclopentadienyl group with formation of metallocene bis-β-diketonates[60,64]:

$$Cp_2MCl_2 + 2NFTA \rightarrow CpM(FTA)_2Cl,\ M = Ti,\ Zr,\ Hf,\ Nb .$$

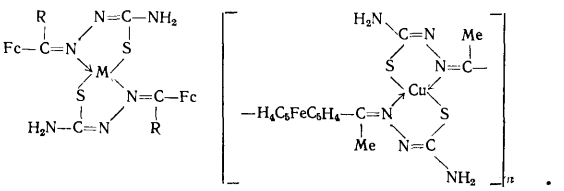
Metallocenes β-diketonates are brightly coloured crystalline substances which are readily soluble in organic solvents, are stable in air, and have relatively high decomposition temperatures.

The isomeric pyridoylferrocenoylmethanates behave unusually in their reactions with copper salts[65]. By virtue of the presence of the pyridine nitrogen atom they form chelates with the ratio Fe : Cu = 1 : 0.6–1 : 3.5 depending on the ratio of the reactants and their concentrations. Several compounds of the type



have been isolated and characterised.

There is also a possibility of the formation of chelates from ferrocene thiosemicarbazones. Copper, nickel, and cobalt chelates based on formylferrocene thiosemicarbazones[66–68], acetylferrocene thiosemicarbazones, and 1,1′-diacetylferrocene bis(thiosemicarbazones) [69] have been obtained:

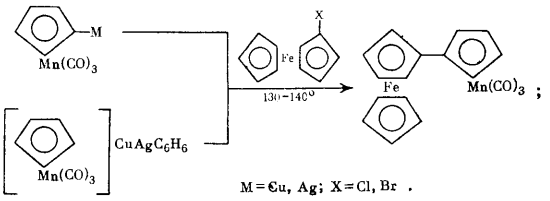


The displacement of the absorption band of the ferrocene fragment in the electronic spectra of these compounds takes place as a consequence of the appreciable mutual influence of the ferrocenyl system and the central metal atom in the complex[57]. Measurements of the magnetic moments have shown that the cobalt complex is a dimer with a Co–Co bond. It has been noted that the coordination of such ligands to metal atoms can occur in the thiol and imine forms[68,70].

Polymeric, infusible, and insoluble in organic solvents chelates of copper, manganese, cobalt, and chromium based on ferrocene-containing β-ketoimines[71–73] and also silver and copper chelate complexes of salicylferrocene[5] have been described. The instability constants of certain organometallic compounds (OMC) of this type have been determined[22].

4. Compounds of the Type Fc–OMC and Fc–R–OMC with σ-Linked Fragments

Various reactions involving the coupling of a cyclopentadienyl ring of ferrocene to groups containing a transition metal entail wide possibilities for the synthesis of HMF. Cymantrenylferrocene—a compound which incorporates the fragments of two of the most thoroughly investigated cyclopentadiene complexes (ferrocene and cymantrene)—has been obtained[74–77]:



M = Cu, Ag; X = Cl, Br .

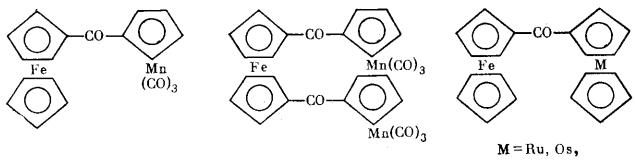
The cymantrenyl substituents can be introduced also into both rings of ferrocene. Cymantrenylferrocene can be obtained by the pyrolysis of diferrocenyl- and dicymantrenylmercury in the presence of silver powder[78]. It has been recently reported[79] that the most convenient method involves the interaction of copper(II) halides with lithiometallocenes. These procedures are also applicable to the synthesis of substituted cymantrenylferrocenes. The yield of the HMF is 30–70%. Cymantrenylferrocene is a stable crystalline substance which is readily soluble in organic solvents and enters into various reactions.

Various HMF can be synthesised similarly from lithio-, sodio-, or other metal-substituted derivatives of one organometallic compound and halogeno-derivatives of another. The synthesis for this procedure of a derivative of tervalent gold, namely dibutylgold thioferrocenolate Fc–SAu–$(n\text{-Bu})_2$, having a trimeric structure, has been described[47]. Diferrocenyldicymantrenyltin has been obtained by the reaction of cymantrenyl-lithium and dichlorodiferrocenyltin. The reaction between ferrocenyl-lithium and dichlorocymantrenyltin also leads to this compound but with a lower yield[80,81]. Under mild conditions, it was possible to obtain ferrocenylmethyl compounds of molybdenum[82] and tungsten[82,83] according to the scheme

$$Fc{-}COCH_2Cl + NaM(CO)_3Cp \rightarrow Fc{-}COCH_2M(CO)_3Cp .$$

The tungsten-containing ketone is stable on storage and in solution in contrast to molybdenum-containing ketone, which decomposes even in the solid state to the extent of one-third in 24 h. Similar HMF and $Fc{-}CH_2Mn(CO)_5$ have been obtained from chloromethyl- and chlorocarbonyl-ferrocene[84,85]. On heating, the carbonyl derivatives are decarbonylated with formation of $Fc{-}M(CO)_3Cp$.

The Friedel–Crafts alkylation and acylation constitute a convenient method of coupling to organometallic fragments[5,7,20,86–89]. A series of HMF of the type



M = Ru, Os,

have been obtained and characterised. The carbonyl groups of these compounds are readily reduced to CH_2 groups with retention of the HMF structure.

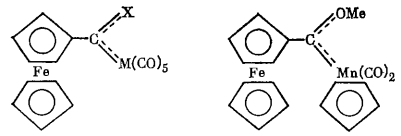
The condensation reactions of aldehyde and ketone derivatives of ferrocene, benzenechromium tricarbonyl, and cymantrene result in almost quantitative yields of the corresponding HMF [90–92] of two types:

RCH=CHCOR′ and RCOCH=CHR′;
R = Fc; R′ = $PhCr(CO)_3$, $C_5H_4Mn(CO)_3$.

Such condensation of ferrocene derivatives has also been achieved with cymantrenylamine and dinuclear ketimines were obtained as a result[22]. The condensation products are crystalline high-melting substances which are soluble in various organic solvents. The manganese derivatives are somewhat less stable in solutions.

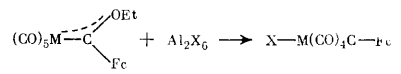
Ferrocenylacetylene can be used to synthesise HMF. Like the synthesis of copper acetylides, the interaction of CuI in aqueous ammonia with ferrocenylacetylene in alcohol[20] leads to copper ferrocenylacetylide (Fe–C≡CCu) in 73–80% yield. Its derivatives dideuterated[93], brominated, and iodinated[94] in the ring have been obtained. Such acetylides can be used successfully in a wide variety of syntheses[13,20,95] including the synthesis of HMF. The exchange reaction of copper ruthenocenylacetylide with iodoferrocene in pyridine gave rise to ferrocenylruthenocenylacetylene[96]: $Fc{-}C{\equiv}CC_5H_4RuC_5H_5$. This compound sublimes *in vacuo* (1 mmHg) at 180 °C without change in its melting point. The reactions of ferrocenylacetylene with *cis*-$PtCl_2(PMe_2Ph)_2$ and $(PPh_3)_2IrCl(CO)$, leading respectively to *trans*-$PtCl(C{\equiv}CFc)(PMe_2Ph)_2$ [97] and a hexacoordinate iridium complex, decomposing on recrystallisation into the initial components, have been described[98].

A series of reactions involving addition to the carbonyl ligand in metal carbonyl have been achieved. The reactions of metal carbonyls with organolithium compounds lead to the conversion of the carbonyl ligand into a carbene ligand. A series of bimetallic ferrocenylcarbene complexes were obtained in the course of studies of a series of ferrocene derivatives[99–101]:



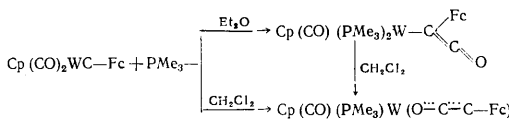
X = OMe, OEt, NH_2, NMe_2, NC_4H_8, $ONMe_4$; M = Cr, W .

These compounds are crystalline, stable in air (with the exception of the manganese complex), and soluble in inorganic solvents. It was not possible to synthesise the analogous cobalt and vanadium complexes. The chromium, molybdenum, and tungsten complexes based on 1,1′-dimethylferrocene were obtained recently[102]. The carbene complexes are the starting materials for the synthesis of new HMF. They react with boron and aluminium halides with elimination of an electron-donating group (one CO ligand), forming carbyne complexes[103,104]:



M = Cr, Mo, W; X = Cl, Br .

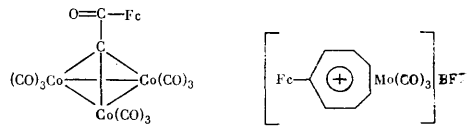
The iodo-homologues have been obtained by the exchange reaction of the above complexes with LiI. The thermal stability of these compounds decreases in the sequence W > Cr > Mo and I > Br > Cl; the chemical stability ranges from that of the iodotungsten derivative, which is stable on storage in air, to the chlorochromium compound, which ignites spontaneously. It has been shown for the tungsten derivative[105] that these complexes react with cyclopentadienylsodium to form dicarbonyl(π-cyclopentadienyl)carbyne complexes, which are readily soluble in organic solvents and whose reactions with phosphines give rise to metal-substituted ketens, which are stable in the solid state[106]:



In CH_2Cl_2 these ketens combine almost quantitatively with CO at 30 atm over a period of 24 h [107] with the formation of $Cp(CO)_2(PMe_3)W{-}C(Fc){=}C{=}O$.

The electrophilic substitution of hydrogen in ferrocene by new acylating agents—carbotricobalt decacarbonyl hexa-

fluorophosphate[108] and the complex $[C_7H_7Mo(CO)_3]BF_4$—has been achieved[7,20], which led to the following HMF:



Other ferrocene cluster compounds have also been obtained: $Fc-CCo_3(CO)_9$ [20,109] and $Fc-CH_2CO_2CCo_3(CO)_9$.[110]

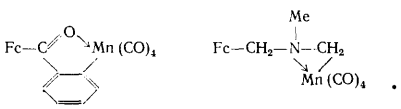
A simple method of synthesis of HMF consists in the addition of organometallic compounds to carbonyl derivatives of ferrocene[21,22,111,112], for example:

$$Fc-CHO \xrightarrow{LiR} Fc-CH(R)OLi \xrightarrow{H_2O} Fc-CH(R)OH,\quad R=C_6H_4Mn(CO)_3;$$
$$Fc-COMe + Cp_2Zr(Cl)H \rightarrow Cp_2Zr(Cl)OCH(Me)-Fc.$$

These compounds are soluble in hydrocarbons but hydrolyse at the metal–oxygen bond with liberation of ferrocene-containing alcohols.

There are literature data concerning polymeric HMF obtained by the copolymerisation of vinyl derivatives of cymantrene and ferrocene[113], (benzyl acrylate)chromium tricarbonyl, and 2-ferrocenylethyl acrylate[114,115]. Polymers of other metal-containing monomers are also known[117–122].

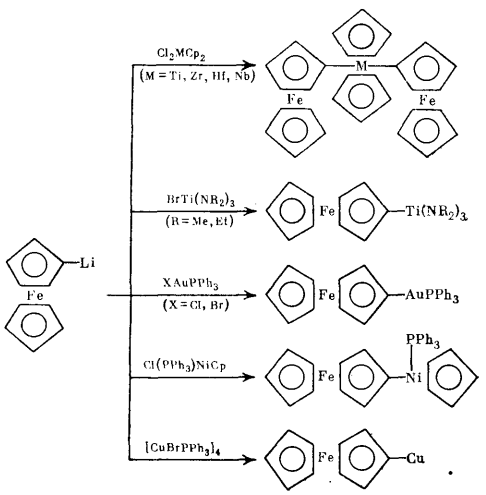
The possibility of the synthesis of HMF by the cyclometallation of substituents in ferrocene derivatives is also noteworthy[127]. Various dinuclear heterometallic derivatives can be obtained by this procedure, but in the case of ferrocene the reaction is known only in a few instances. These involve the metallation of benzoylferrocene and dimethylaminomethylferrocene with methylmanganese pentacarbonyl in the benzene ring and in the methyl group respectively[128]:



Pyrazolines containing the ferrocenyl and cymantrenyl substituents have been described[116,129]. Catalytic thermolysis of such pyrazolines in the presence of KOH and platinum on charcoal leads to the corresponding cyclopropane HMF.[116]

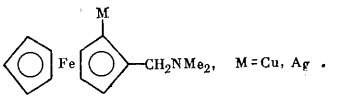
5. Compounds With a Cyclopentadienyl–Metal Bond

HMF of this kind are usually obtained by the exchange reaction between lithioferrocenes and transition metal halides[130–137]:



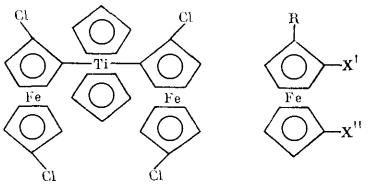
The reaction with $AuCl_3$ terminates with the formation of HMF in satisfactory yield only for the ratio Li : Au = 2 : 1.[133] Only the compound $Fc_2AuClPPh_3$ has been obtained under these conditions.

The thermal stability of HMF of this type varies within wide limits—from the nickel compound which is unstable in a pure form[135,136] to the cyclopentadienyl derivatives of Group IV metals which sublime *in vacuo* at high temperatures[130,131]. However, the latter are unstable in air. Ferrocenylcopper, which in unstable in an inert atmosphere up to 120 °C, also decomposes in air. It is noteworthy that the presence of halogen atoms and of the dimethylaminomethyl group in the cyclopentadienyl rings of ferrocene stabilises the carbon–metal bond and the HMF is also much more stable. Thus the HMF obtained from 1-(dimethylaminomethyl)-2-lithioferrocene and copper and silver iodides (yield more than 60%) are stable in air up to 150–170 °C:[138,139]



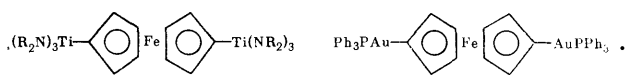
Similar methoxy-substituted HMF are somewhat less stable[140].

Copper and silver derivatives without stabilising substituents were obtained only recently[137,141]. The silver derivative is more stable and persists in air for several hours. A series of derivatives of other metals have been obtained from lithioferrocenes containing stabilising substituents:[142,143]

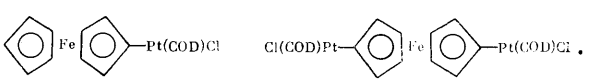


$X^I = X^{II} = Cl$, $R = Mn(CO)_5$, $AuPPh_3$, $Ir(CO)PPh_3$;
$X^I = Cl$, $X^{II} = H$, $R = AuPPh_3$.

If 1,1′-dilithioferrocene is used in the synthesis, HMF substituted in both rings are obtained[132,142,144,145], for example:

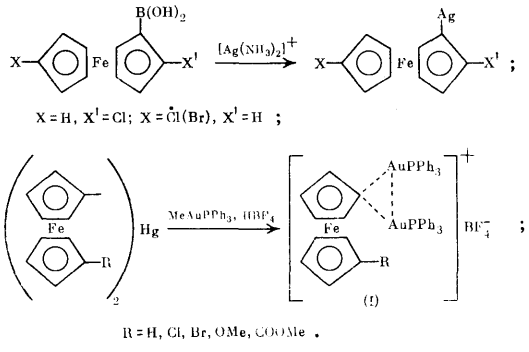


The same results were obtained on incomplete ferrocenylation of the platinum salt $Pt(COD)Cl_2$ (COD = cyclo-octa-1,5-diene) with trimethylstannylferrocene and 1,1′-bis(trimethylstannyl)ferrocene[146]:

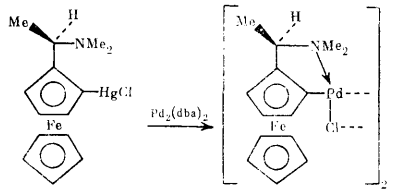


The reaction of 1,1′-dilithioferrocene with cobalt chloride leads to the formation of polyferrocenylenes[147].

Apart from the organolithium and organotin compounds, ferrocene derivatives of boron[148–151] and mercury[152–156] are used for the synthesis of HMF of this type:

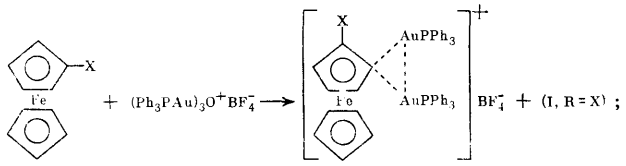


These reactions involving organomercury compounds proceed over a period of several minutes at room temperature with yields of compounds (I) up to 80–90%. The use of the optically pure 2-chloromercuri-derivative of 1-dimethylaminoethylferrocene for the synthesis of an optically active complex with a palladium atom in the ring has been described[157–159]:



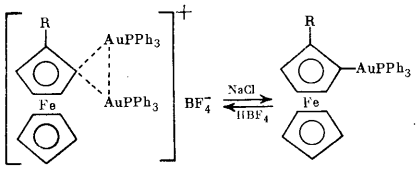
where dba = dibenzylideneacetone.

Other methods of adding a transition metal directly to a cyclopentadienyl ring of ferrocene are also known. Nesmeyanov and coworkers[160–163] were the first to metallate ferrocene and its derivatives by an aurating agent—a gold-containing oxonium salt. Ferrocene is aurated at 20 °C in the presence of HBF_4, giving a 60% yield of a cationic digold complex (I, R = H). Ferrocene derivatives form mixtures of homoannular and heteroannular isomers:



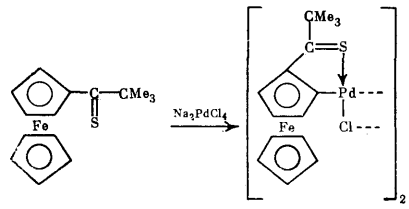
X = Me, Ph, $C_6H_4NO_2$, COMe, Cl .

In all cases, except when X = Ph, homoannular 1,2-isomers are formed preferentially. Methoxy- and nitro-ferrocenes give rise to 1,2-disubstituted ferrocenes only. Under the influence of nucleophiles (Cl^-, CN^-, PPh_3), the cationic complexes are converted quantitatively into organomonogold compounds, whose reaction with tetrafluoroboric acid readily reconverts them into ionic complexes[164]:

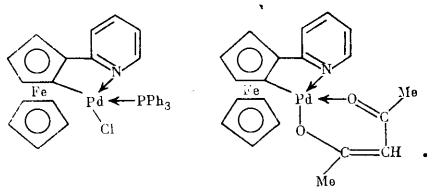


The reaction proceeds from right to left also under the influence of dinuclear organogold complexes $[R(AuPPh_3)_2]BF_4$.[165] In view of the ease of such reactions, it is assumed that it is most convenient to synthesise gold-containing HMF of the type $Fc–AuPPh_3$ from organomercury compounds via the cationic complexes[155]. It is of interest that acetylferrocene is aurated by tris(triphenylphosphinegold)oxonium permanganate not in the cyclopentadienyl ring but in the acetyl group, forming $Fc–COCH_2AuPPh_3$, albeit in a low yield (5%).[161,162]

The first example of the intramolecular orthopalladisation of metallocenes was published in 1974:[166]

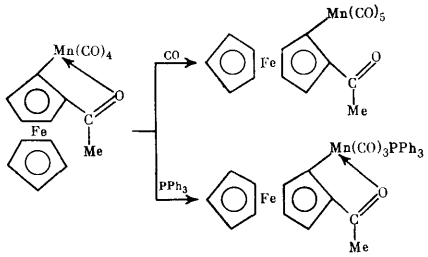


Subsequently this reaction was achieved also for other ferrocene derivatives—dimethylaminomethylferrocene[167], 2-pyridylferrocene[168], acetylferrocene *N,N*-dimethylhydrazone[169], acetylferrocene acetylhydrazones[170], and 1,1′-diacetylferrocene bis(acetylhydrazone).[171] Li_2PdX_4 (X = Cl or Br) are also used as palladising agents. The reaction is carried out in the presence of sodium acetate. The dimeric complexes obtained in a yield exceeding 90% react with electron-donating molecules or metal acetylacetonates to form the corresponding monomeric HMF, for example;



If the palladisation is carried out in the presence of a salt of an optically active acid or an optically active derivative of ferrocene is used, then optically active HMF are obtained. The asymmetric cyclopalladisation of dimethylaminomethylferrocene [172,173] and the optically active *N,N*-dimethylamino-1D-methylferrocene [174] and 1-dimethylaminoethylferrocene[157,158] has been achieved.

The metallation of acetyl- and dimethylaminomethyl-ferrocenes by methylmanganese and methylrhenium pentacarbonyls has also been described[128,175]. In all cases homoannular *ortho*-metallated ferrocenes are formed in 32–50%, yield except in the reaction of dimethylaminomethylferrocene with the manganese compound described in the previous section. The reaction of the manganese derivative with CO is accompanied by ring rupture, which indicates the lability of the Mn ← O bond; however, the reaction with triphenylphosphine proceeds differently—with substitution of one carbonyl group:

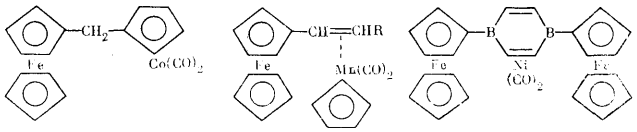


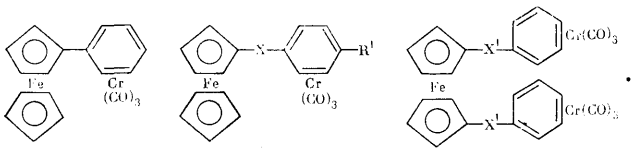
6. π-Complexes of Unsaturated Ferrocene Compounds

Heterometallic derivatives of ferrocene can be obtained from metal carbonyls using the ability of the latter to substitute their CO groups by π-donor ferrocene-containing ligands. Several compounds of this type have been described. Ferrocenylacetylenes readily react with cobalt carbonyl[26,98]:

$$Fc{-}C{\equiv}CR + Co_2(CO)_8 \xrightarrow{C_6H_6,\,25^\circ} Fc{-}C{\equiv}CR\,[Co_2(CO)_6]\ ;$$
$$R=H,\ Fc\ .$$

The following cobalt-, manganese, nickel-, and chromium-containing HMF have been obtained similarly (sometimes with ultraviolet irradiation): [20,85,176–180]

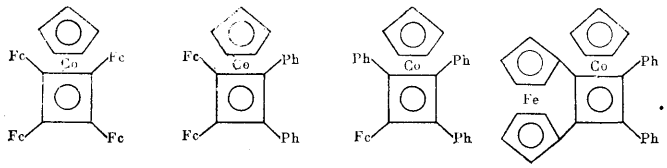




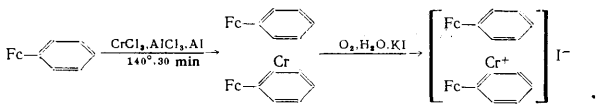
(a) R = H, Me; (b) R' = H, X = CH_2, CO, CH_2CH_2, $COCH_2$, CH(OH)CH_2, CH=CH, CH(OH); (c) R' = Me, X = CO, CH(OH); (d) X' = $COCH_2$, CH(OH)CH_2 .

Cobalt- and manganese-containing HMF of this type are relatively readily fusible compounds (or liquids); the chromium-containing HMF and the nickel complex melt (sometimes with decomposition) in the range 135–230 °C.

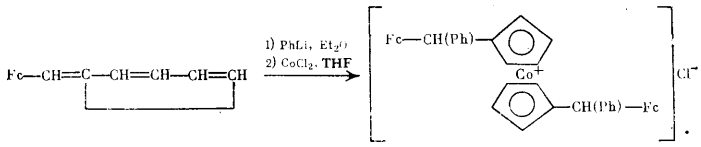
The interaction of the ethynylferrocenes Fc–C≡CPh, Fe–C≡C–Fc, and Fe($C_5H_4C{\equiv}CPh)_2$ with the cyclopentadienylcobalt complexes $CpCo(CO)_2$, $CpCo(PPh_3)_2$, and CpCo(RC≡CR)PPh_3 have been studied by two groups of investigators[181,182]. Mixed cyclobutadiene complexes with different Fe : Co ratios, soluble in hydrocarbons, were isolated:



The group of compounds which are synthesised using arene- or cyclopentadienyl-containing metallocenes, usually ferrocenes, while the other metal is introduced, by the method for the synthesis of metallocene and arene compounds, should be assigned to this type of HMF. Thus, 1,1'-diferrocenyldibenzenechromium, identified as the iodide, has been synthesised under the conditions of the Fischer reaction in 17% yield[123]:



Since the synthesis is complicated by side reactions, an attempt was made to synthesise this compound and its *p*-tolylferrocenyl analogue by the reaction of chromium vapour with phenyl- and *p*-tolylferrocene in a high vacuum (10^{-5} mmHg, 77 K); the yield was approximately 1% relative to the evaporated chromium, which entered the reaction zone[124]. A similar cobaltocenium derivative was obtained from α-ferrocenylfulvene[20]:



The manganese[125] and tungsten[126] derivatives have been obtained analogously.

Dimeric 1-ferrocenyl-π-allylpalladium chloride complexes have been synthesised by the reaction of conjugated dienes (butadiene, isoprene, and 2,3-dimethylbutadiene) with ferrocenylpalladium chloride, obtained *in situ* from chloromercuriferrocene and Li_2PdCl_4.[183] A complex of vinylferrocene and palladium(II) chloride has also been obtained[33].

7. Transition Metal Complexes with Ferrocene Ligands Containing Group V and VI Elements as Donor Atoms

The complex formation reactions of ferrocene derivatives containing electron-donating nitrogen, phosphorus, arsenic, etc. atoms with transition metal compounds constitute a convenient method of synthesis of HMF. Thus, when dimethylaminomethylferrocence is mixed with nickel and cobalt halides and thiocyanates[184] and also with palladium chloride[185], solid coloured adducts are formed:

$$[FcCH_2NMe_2]_2MX_2 \quad M=Co,\ Ni,\quad X=Cl,\ Br,\ I,\ CNS;\quad M=Pd,\ X=Cl\ .$$

The reaction with titanium and zirconium halides gives rise to 1 : 1 complexes[186]. Dimethylaminomethylferrocene hydrochloride reacts with K_2MCl_4 and $Na_2M(CN)_4$, yielding compounds with a different structure[185]: $[FcCH_2NHMe_2]_2MX_4$, where M = Pt or Pd. Nickel, platinum, palladium, ruthenium [187], and rhodium[188] complexes of 1,1'-bis(dimethylarsino)ferrocene[187,188] and 1,1'-bis(diphenylarsino)ferrocene[187], the palladium complex of 2-ferrocenylpyridine[168], the nickel[189], cobalt[190], gold[191], and palladium[192] complexes of ferrocenylphenylphosphines, the cobalt, nickel, and copper complexes of 1,1'-bis(diphenylphosphino)ferrocene [193], the rhodium complexes of ferrocenylphosphinamines[194], the cobalt complex of 1-(dimethylaminomethylmethyl)-2-pyridylferrocene[26], the titanium and zirconium complexes of ferrocenylacetonitrile[186], the silver[39], titanium, and vanadium[39,195] complexes of 1,1'-dicyano-ferrocenes[7,22], and the ruthenium complexes of cyanoferrocene and ferrocenylacrylonitrile[196] have been synthesised and investigated.

Ferrocenylphosphinegold halide complexes are converted into organogold HMF under the influence of organolithium and organomagnesium compounds[197]

$$BrAuL + MeMgI \rightarrow MeAuL\ ;$$
$$L = PFc_3,\ FcPPh_2\ .$$

Oxidants react with these complexes in a way which depends on the nature of the reagent[191], oxidising either gold or the ferrocene system:

$$BrAuFcPPh_2 \xrightarrow{Br_2} Br_3AuFcPPh_2$$
$$BrAuFcPPh_2 \xrightarrow{HAuCl_4} [(BrAuFcPPh_2)^+(AuCl_4)^-]_3Au\ .$$

Triferrocenylphosphine complexes of arylgold compounds are obtained by displacing triphenylphosphine with triferrocenylphosphine, the latter being a stronger electron donor[197]:

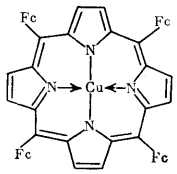
$$ArAuPPh_3 \xrightarrow{Fc_3P} ArAuPFc_3\ ;$$
$$Ar = p\text{-}MeC_6H_4,\ m\text{-}FC_6H_4\ .$$

HMF of this type are also known to include cationic digold complexes[165,197,198], which are formed, like the compounds

aurated in the ferrocene nucleus, via the following mechanisms:

$$R_2Hg + MeAuPFc_3 \xrightarrow{HBF_4} R(AuPFc_3)_2BF_4,$$
$$R=PhCH=CH,\ PhCH=C(COOMe),\ o\text{-}IC_6H_4,\ \alpha\text{-thienyl};$$
$$p\text{-}MeC_6H_4AuPFc_3 \underset{Fc_3P}{\overset{HBF_4}{\rightleftarrows}} p\text{-}MeC_6H_4(AuPFc_3)_2BF_4.$$

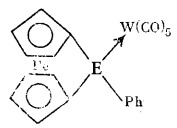
The first heterometallic derivative of ferrocene of the porphyrin series has also been obtained from *meso*-tetraferrocenylporphyrin and copper acetate in dimethylformamide and has been isolated after recrystallisation from chloroform in the form of an adduct with dimethylformamide and $CHCl_3$:[199]



According to Mössbauer spectroscopic data, oxidation of this compound results in the formation of several ferrocenium centres.

A series of HMF have been obtained by the reactions of metal carbonyls with ferrocenylphosphine ligands: $CpMn(CO)_2L$ (L = PFc_3, PFc_2Ph, or $PFcPh_2$), $RC_5H_4Mn(CO)_2PFc_3$ (R = Et, C_5H_{11}, MeCO, or C_4H_9CO), $C_6H_6Cr(CO)_2L$ and $(CO)_5ML$ (M = Cr, Mo, or W), $(CO)_4ML_2$ (M = Mo or W), $Fc_3PMn_2(CO)_9$, $[(FcPPh_2)_2Co(CO)_3]^+BPh_4^-$,[190,200–203] and $Fc_3PMn(CO)_4Me$.[128] Similar complexes of chromium, molybdenum, tungsten, vanadium, cobalt, and nickel carbonyls with bifunctional nitrogen-, phosphorus-, and arsenic-containing ferrocene ligands have been described[193,194,204,205].

It is known that coordination to transition metals appreciably stabilises ligands which are relatively unstable under the usual conditions. It is therefore possible to employ in the synthesis of stable HMF of this type even ferrocene compounds which are unstable in air. For example, crystalline complexes stable in air have been obtained from thioketones which readily polymerise and oxidise under the usual conditions and from ferrocenophanes, which are unstable in air[206–208]:



$Fc{-}CS{-}CMe_3Cp_2Mo_2(CO)_4$
$Fc{-}C(R){=}S \rightarrow M(CO)_5$;
R=Ph, M=Cr, Mo, W; R=Me, M=W;
E=P, As.

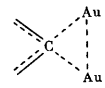
The possibility of synthesising HMF of this type by displacing amine ligands from the Reinecke salt by aminoferrocenes (L) has also been demonstrated[209]. With a 1 : 1 component ratio, the outer-sphere ammonia is displaced with formation of the solid crystalline complex $LH[Cr(SCN)_4(NH_3)_2]$. With increase of the aminoferrocene : Reinecke salt ratio, the inner-sphere ammonia is displaced.

III. STRUCTURE AND PROPERTIES

1. Structure

The structural analysis of crystalline HMF has been carried out for certain compounds, which made it possible to discover their structural characteristics. When a metal forms σ-bonds directly with a carbon atom of a cyclopentadienyl ring of ferrocene, there is a possibility of a redistribution of electron density with participation, in particular, of the metal *f* orbitals, which alters the interatomic distances in the Fc fragment[138]. On the other hand, in the case of diferrocenyltitanocene Cp_2TiFc_2, a shortening of the σ-bond between titanium and a carbon atom of the cyclopentadienyl ring of ferrocene and constancy of the bond lengths in the sandwich fragments were observed[210]. The molecular structure of $(Et_2N)_3TiC_5H_4FeC_5H_4Ti(NEt_2)_3$ has been described[211].

There is also a possibility of a more complex bonding of the metal atom to the cyclopentadienyl ring with formation of the structural fragment



in which the two gold atoms linked to one another form a three-centre two-electron bond with one of the carbon atoms with the ferrocene-containing group[154,164]. The presence of the above fragment has been most clearly confirmed by X-ray diffraction data for the compound $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)Au_2.(PPh_3)_2]BF_4$.[212,213]

The Au–Au bond (2.77 Å) in such compounds is shorter than in metallic gold (2.88 Å). As a consequence of the presence of the Fe–Au bond (2.82 Å), the planes of the cyclopentadienyl rings are not parallel (the dihedral angle is 16°) and the bridging ring has the envelope configuration. Ultraviolet spectroscopic and ^1H NMR data show that the bridge structure of the compounds is maintained also in solutions[153,214]. The related compound 2-copper(dimethylaminomethyl)ferrocene and its silver analogue have the cluster structure[215,216]. In these substances it is also possible to isolate the fragment



but the distortion of the Fc is smaller probably due to the weaker interaction between M and Fe. A weak interaction between the silver atom and the nitrogen atom of the aminogroup has been noted for the silver derivative.

Direct bonding of the metal to a carbon atom of a cyclopentadienyl ring of ferrocene is not always accompanied by the M–Fe interaction. Apart from the nature of the atom M, the character of the bonds which it forms with the atoms in the immediate environment is of decisive importance. For example, in cyclo-1-(1′-dimethylaminoethylferrocene)-2-(acetylacetonato)palladium the metal is involved in the square planar coordination fairly characteristic of palladium with formation of acetylacetonate and PdC_3N metal-containing rings. The ferrocene fragment has a configuration intermediate between crossed and eclipsed with the usual average bond lengths[159].

In the absence of a direct bond between M and a cyclopentadienyl ring of ferrocene, the mutual influence of the M and Fe atoms on the structural characteristics of their environment is also weakened. However, it is still fairly pronounced, for example, in halogenotetracarbonyl complexes of transition metals bound to the ferrocenyl residue by a linkage of the type $M{\equiv}C{-}Fc$.[104] In these compounds, as in the carbene derivatives which resemble them[102], there is a significant decrease of electron density in the cyclopentadienyl rings of ferrocene as a result of the stronger conjugation than in the usual substituted ferrocenes, caused by the overlap of the π orbitals of the substituted ring by the p_z orbital of the acetylenic carbon. The HMF considered are oxidised more readily than ferrocene; their oxidation-reduction properties are appreciably influenced by the nature of the metal and to a lesser extent the halogen.

The compound of nickel iodide carbonyl with ferrocene-1,1'-bis(dimethylarsine) [217] is of interest because in it the cyclopentadienyl rings of ferrocene form part of a bidentate ligand. The nickel atom has a trigonal bipyramidal coordination with the equatorial and axial dispositions of As. The $FeAs_2$ and $NiAs_2$ planes form an angle of 46.6° and the cyclopentadienyl rings are rotated by 8.8° compared with the eclipsed conformation and are inclined to one another at an angle of ~3°. The Ni–As distances are within the usual limits for nickel complexes with arsenic derivatives, but the equatorial bond is somewhat longer than the axial bond. The interatomic distances in the ferrocene fragment have the usual values. The C–O bond is shorter than in the carbonyl complexes. The bidentate ligand may include also one cyclopentadienyl ring of ferrocene. It has been established by NMR and infrared spectroscopy[204] that 1-(dimethylamino)-methyl-2-(diphenylphosphino)ferrocene behaves as a bidentate ligand in reactions with Group VI metal (Cr, Mo, and W) carbonyls and gives rise to a complex of the type $[CpFeC_5H_3.(PPh_2)CH_2NMe_2]W(CO)_4$.

Polydentate ligands can also be linked with the aid of the ferrocene fragment. This can entail the formation of strained structures. Comparison of the EPR spectra of copper chelate complexes of acetylacetone, ferrocenylacetone, and 1,1'-bis-acetoacetylferrocene showed that only in the latter case does the symmetry of the environment of the copper ion deviate from the acetylacetonate symmetry[50,51]. When the ferrocene nucleus is separated from the M atom by two and more atoms, the mutual influence of the metal-containing fragments on their structure is not observed. In such complexes ferrocene frequently has the eclipsed conformation[182,218]; however, as in the cases discussed above, the conformation may be influenced decisively by the packing in the crystal and not by the electronic structure and geometry of the molecule. Estimation of the mixing coefficients in the molecular orbital of the unpaired electron showed that these coefficients of the $d_{x^2-y^2}$ orbitals of the copper atoms are identical to within 0.04 for the acetylacetonate and ferrocenoylacetonate. This indicates identical distibution of spin density in a type b_1 orbital in both chelates and the absence of an appreciable influence of the ferrocenyl substituent on this orbital[51]. The ferrocenyl residue also does not have a significant influence on the metal atom in the tetraferrocenylporphyrin complex; the EPR spectrum corresponds to the spectra of other copper complexes of porphyrins[199]. The usual structure of the chelate unit has been found also in other metal ferrocenoylacetonates[51,56]. However, a redistribution of electron density can occur in orbitals without unpaired electrons[219,220].

The nature of the localisation of the charge in the ferrocene component is most significant in ionic compounds. If the ferrocene component consists of a ferrocenium type cation, then the Fe–Cp bonds in it are weakened (compared with the corresponding ferrocene derivative) and the absorption bands in the infrared spectrum corresponding to these bonds undergo a bathochromic shift[27,30]. Allowance for this and also for the bathochromic shift of the d–d transition band in the optical spectrum led to an ionic structure for complexes of ferrocene with metal halides[36,37].

2. Solubility

There are no quantitative literature data on the solubilities of HMF (with a rare exception[56]). Only qualitative data are usually quoted, from which it follows that many HMF are appreciably soluble in organic solvents. In order to increase the solubility of compounds based on β-diketones in hydrocarbons, the oleic acid residue is introduced into the molecules of the β-diketonates[221]. The low solubility of salts of nitrogen-containing ferrocene chelates[65,69] and acids[45,46] is apparently associated with intermolecular association in the solid state via the electron-donating nitrogen atoms or with the polymeric structure of the compounds. HMF of other types are apparently also insoluble due to their polymeric structure[5,47,63].

3. Thermal Stability

Polymerisation in the solid state influences appreciably the thermal behaviour of HMF. For example, polymeric chelates of ferrocene thiosemicarbazones and β-ketoimines[66–69,71] do not melt up to 250–300 °C, decomposing in the solid state on further heating. The unusually high stability of ferrocene-silver compared with alkyl- and aryl-silver can also be accounted for by the formation of intermolecular bonds[151].

The thermal decomposition of HMF has been investigated for a few compounds. Thermolysis of ferrocenium salts has been investigated for the reineckate and salts with isopoly-acids[28–30,49]. A characteristic feature of the process is the formation of ferrocene. The thermal stability of salts of ferrocenemonosulphonic acid has been characterised by thermogravimetric and differential thermographic methods[43]. The compounds are unstable in air in the anhydrous state, the copper salt decomposing even before the loss of the entire water of crystallisation.

The thermal decomposition of the copper chelate of ferrocenylacetone has been investigated by derivatographic, mass-spectrometric, and gas-chromatographic methods[49,51]. It has been established that cyclopentadiene, methane, and hydrogen are evolved at 200–260 °C together with a keto-derivative of ferrocene (identified by the infrared spectra); the residue contains metallic copper and iron(II) and iron(III) oxides. The chelates of ferrocene-containing β-ketoimines decompose in the same temperature range (>200–250 °C),[73] their thermal stability being lower than that of the initial β-ketoimines, which the authors attribute to the presence of the unstable ferrocenium form in the polychelates.

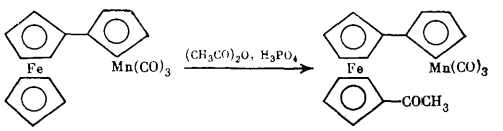
There exist data on the thermal stabilities and decomposition of other compounds, in particular the copper salt of ferrocenecarboxylic acid[22], allylpalladium ferrocenyltrifluoro-acetonate[59,60], 2-copper-1-(dimethylaminomethyl)ferrocene[215], a series of ferrocenesilver compounds[148–150], diferrocenyl-dicyclopentadienyl derivatives of titanium, zirconium, hafnium[130], and niobium[131], and also ferrocenephosphinegold cationic complexes[197]. The majority of HMF lose the ability to sublime on heating which is characteristic of ferrocenes. One of the few exceptions to this rule is ferrocenylruthenocenylacetylene[96] and the dicyclopentadienyldiferrocenyl derivative of zirconium, hafnium, and titanium[130] (the heat capacity of the last compound was measured and its thermodynamic functions were calculated[222]).

4. Chemical Properties

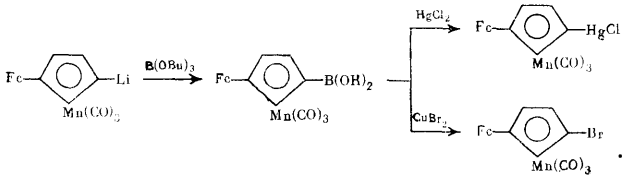
The majority of HMF are resistant to oxygen and atmospheric moisture, except for the compounds mentioned in the appropriate parts of the review. The instability of individual HMF in organic solvents has also been pointed out[33,60,64,102,105,133,161,205].

Many HMF exhibit an important chemical property of ferrocene—the ability to be oxidised to the cation[87–90,178,180,223], which may serve as one of the ways of synthesising trimetallic compounds[128,129]. Both organometallic fragments of HMF are chemically reactive. For example, depending on

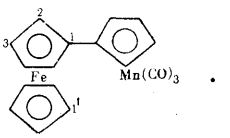
the type of reagents employed, the substitution of a hydrogen atom in cymantrenylferrocene can take place in a cyclopentadienyl ring of either ferrocene or cymantrene. Acylation by acetic anhydride proceeds in accordance with the mechanism[76,77]



In contrast to this, metallation by n-butyl-lithium occurs in the cyclopentadienyl ring of cymantrene. The organolithium derivative obtained is a convenient reagent for the synthesis of various derivatives of ferrocenylcymantrene containing substituents in the cymantrene ring:

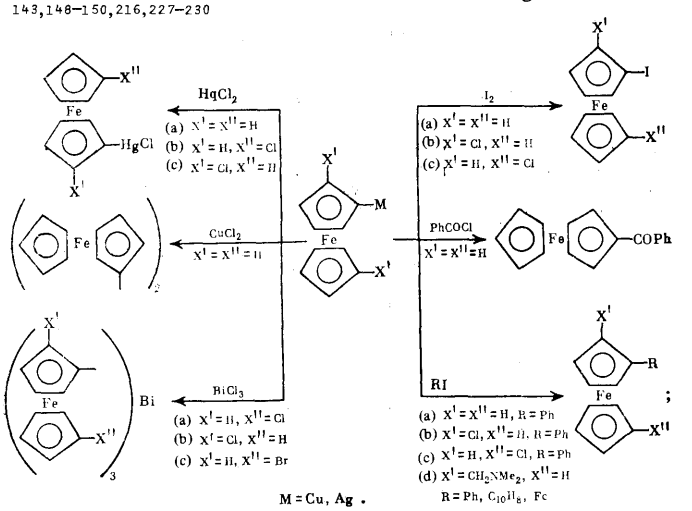


The bromo-derivative of this HMF, containing bromine in a cyclopentadienyl ring of ferrocene, can be obtained from 1,1'-dibromoferrocene and cymantrenylcopper or cymantrenylsilver via the reactions described above (in Section II). Bromine can be substituted by other groups on treatment with bivalent copper salts (acetate and phthalimide)[75,77]. Thus the properties of the σ-linked cymantrenyl and ferrocenyl residues in cymantrenylferrocene differ from those of cymantrene and ferrocene. The difficulty of the exchange of the bromine in 1-bromo-1'-cymantrenylferrocene for different groups, the ease of reduction of the ferrocene derivative to cymantrenylferrocene, the smaller tendency of the latter (compared with ferrocene) to undergo oxidation to the ferrocenium cation, the reduced basicity of 1-amino-1'-cymantrenylferrocene (compared with ferrocenylamine), and also its oxidation to the corresponding azoferrocene, which takes place with difficulty, are associated with the electron-accepting influence of the cymantrenyl group. This has been confirmed by the formal oxidation-reduction potentials[223,254] and data for the isotope exchange of the hydrogen in cymantrenylferrocene with acids[225], from which it follows that the cymantrenyl substituent decreases the rate of the isotope exchange involving the ferrocene nucleus by a whole order of magnitude and that the most reactive positions for electrophilic substitution are 1' and 3:



It was established that the 1'-, 3-, and 2-positions are respectively 8 times, 11 times, and 20 times less active than in ferrocene. It is significant that, under the conditions of the hydrogen isotope exchange, the cymantrenyl fragment does not react. The result of the study of the isotope exchange involving benzenedicarbonyldiferrocenylphosphinechromium[226] is unexpected—the hydrogen atoms of the π-benzene and cyclopentadienyl rings are exchanged at almost the same rates, indicating the equalisation of the electron density in the given complex. The hydrogen atoms of the cyclopentadienyl rings in Ph_2PFc, coordinated to the chromium atom, undergo isotope exchange faster almost by three orders of magnitude than the hydrogen atoms of the non-coordinated ferrocenylphosphine.

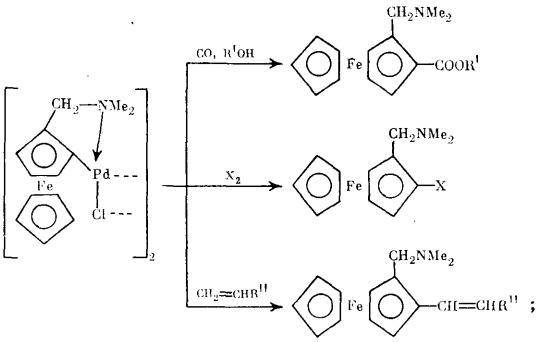
Many HMF with a metal–carbon σ-bond readily react with various reagents, which can be used for the synthesis of ferrocene otherwise difficult to obtain, including HMF:[137,140,143,148–150,216,227–230]



M = Cu, Ag .

The reactions of the organonickel σ-complexes $CpFeC_5H_3$.(Cl)$Ni(PPh_3)Cp$ with acids, acetyl chloride, and mercury(II) chloride also take place under mild conditions and with high yields[135,136]. The nickel–π-cyclopentadienyl ring and nickel–triphenylphosphine bonds are not involved in this process. The organogold derivatives $Fc-AuPPh_3$ react with halogens also with formation of halogenoferrocenes and triphenylphosphinegold halides[231,232]. However, reactions involving the electrophilic substitution of the gold atom could not be carried out[233]. The high reactivity of the gold–carbon bond has been used to synthesis the substituted vinylferrocenes Fc–C(CN) = C(CN)R, where R = CN or $AuPPh_3$.[234] Hydrogen sulphide and the acids HX (X = Cl or Br) readily decompose many similar HMF.[42,130,131,141,148–150] Stabilised ferrocenylsilver and ferrocenylcopper condense with cymantrenylcopper and chloroferrocenylsilver above 120 °C, forming dinuclear metallocenes[216].

It has been shown for various aminoferrocenes with a Pd atom in the ring that extensive synthetic possibilities are associated with HMF of this type. The reaction conditions depend greatly on the nature of the reagent; the products of the synthesis are 1,2-substituted ferrocenes[168,235,236]:

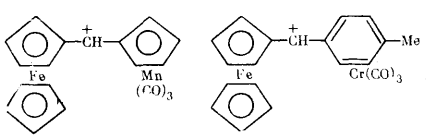


R'=H, Me; X=Br, I; R''=Me, Ph, CN, COOMe, etc.

Such reactions have also been achieved for similar enantiomeric HMF.[172,235,237–239] The latter are planar-chiral compounds and substitution of the metal by some other group takes place with retention of not only the stereochemical configuration but also of the enantiomeric purity. The presence in these HMF of the dimethylamino-group, which tends to

undergo nucleophilic substitution in the form of a quaternary ammonium base, makes it possible to vary within wide limits the nature of the substituents and to obtain a wide variety of 1,2-disubstituted ferrocenes.

The marked influence of the organometallic fragment linked to the ferrocene fragment on the properties of the latter is also illustrated by the behaviour of the α-metallated ketones $Fc-COCH_2M(CO)_3Cp$ (M = Mo or W) in relation to nucleophiles[83,240]. In contrast to acetylferrocene, such HMF do not form derivatives involving the keto-group. This is associated with the low electrophilic activity of the carbon atom of the keto-group, caused by the marked electron-donating properties of the cyclopentadienylmetal carbonyl fragments, and also with the dissociation of the metal–carbon σ-bond in reactions with nucleophiles. Triethyloxonium tetrafluoroborate converts these ketones into the corresponding salts $[Fc-C(OEt)CH_2M(CO)_3Cp]BF_4$, which are convenient reagents for the synthesis of derivatives of α-metallated ketones. α,β-Unsaturated ketones, for example, ferrocenylideneacetylcymantrene, react with methylmagnesium iodide via the 1,2-addition mechanism to form the corresponding ketone and tertiary alcohol[92]. The latter is converted under the influence of HBF_4 in acetic anhydride into a salt of the allyl cation, which alkylates dimethylaniline in the *para*-position with an almost quantitative yield of the derivative $Fc-CH.(C_6H_4NH_2)CH=C(CH_3)C_5H_4Mn(CO)_3$. Secondary and tertiary carbinols of this type readily ionise on treatment with acids, forming intensely coloured carbenium ions[179,241,242]:



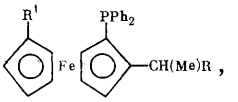
Such cations are extremely stable owing to the delocalisation of the positive charge over both metallocenyl residues.

Finally, the high reactivity of the carbene complexes $(CO)_5CrC(Fc)X$, where X = OMe or NC_4H_8,[218,243] and of ferrocenylpalladium chloride obtained *in situ*,[244,245] which produce various linear and cyclic ferrocene derivatives in reactions with unsaturated compounds, is noteworthy. The reactions involving other types of HMF have been little studied. In contrast to palladium chloride, ferrocenium trichloropalladate reacts with allyl chloride, forming the complex $(C_3H_5)_2Pd_3Cl_4$.[246] Reactions involving the addition of neutral molecules (CO, SO_2, MeSCN) to the rhodium complexes of 1,1′-bis(dimethylarsino)ferrocene (AF) of the type $[Rh(AF)_2]PF_6$ to form the complexes $[Rh(L)(AF)]PF_6$, which in their turn combine with various molecules X (X = H_2, O_2, Br_2, I_2, HCl, HBr, HI, MeI, $MeSO_2Cl$, $F_3CC{\equiv}CCF_3$, or MeSSMe), forming the compounds $[RhX(AF)]PF_6$, have been described[188]. The compound $[Rh(S_2)(AF)_2]PF_6$ has been obtained by the reaction with sulphur, while the reaction of $[Rh(O_2)(AF)_2]PF_6$ with SO_2 yields $[Rh(SO_4)(AF)_2]PF_6$.

IV. APPLICATIONS OF HETEROMETALLIC DERIVATIVES OF FERROCENE

In contrast to ferrocene and benzenechromium tricarbonyl, the ferrocenylcarbene complexes of chromium are catalysts of the hydrogenation of nitriles and amides to amines[100]. The hydrogenation of olefins does not occur under these conditions. The hydrogenation of various unsaturated compounds in the presence of chiral ferrocenylphosphinerhodium complexes is used to obtain optically active compounds[247–251].

Derivatives of the type



R = H, OH, NMe_2; R′ = H, PPh_2

are used as a rule of the chiral ligand.

The hydrogenation of α-acetamidoacrylic acids takes place with a yield of 86–94%.[194,248,252] The process takes place in various solvents with a high stereoselectivity (the optical yield is 89–93%). Acetophenone is hydrogenated rapidly and quantitatively to (*R*)-1-phenylethanol with an optical purity of 40%,[253] which is much higher than in the presence of other known rhodium catalysts of this process. The biologically active 2-amino-1-arylethanols are obtained by the hydrogenation of aryl aminomethyl ketones with 100% conversion and an enantioselectivity up to 95%.[249] Phosphine complexes of rhodium without ferrocenyl substituents exhibit a lower activity (80% conversion) and a lower optical yield (12%).

Dichloro[1,1′-bis(dimethylphosphine)ferrocene]nickel(II) catalyses the hydrosilylation of olefins and acetylenes[254,255]; in some cases this entails the substitution of hydrogen by chlorine. The hydrosilylation reaction is catalysed also by a platinum complex of this type. The asymmetric hydrosilylation of olefins, catalysed by chiral ferrocenylphoephine-palladium complexes[256], is used for the synthesis of optically active alcohols and alkyl bromides. A series of chiral phosphineferrocenerhodium complexes have been used successfully for the asymmetric hydrosilylation of ketones[257]. These HMF can give rise to hydrosilylation products with a higher optical yield than the phosphinerhodium complexes without ferrocene. Ferrocenylphosphinerhodium complexes are also effective catalysts of the hydroformylation of unsaturated compounds[258,259]. For example, the hydroformylation of hex-1-ene to n-hexanol takes place with 100% conversion and 93.2% selectivity.

The complex $(Ph_2PC_5H_4)_2FePdCl_2$ is the most active of the nickel and palladium complexes of phosphines in reactions of s-alkyl Grignard reagents with organic halides[260] and allyl alcohols[261]. The corresponding secondary derivatives are obtained as a result in a high yield (up to 97%). The reactions are not complicated by the isomerisation of the secondary alkyl groups to the primary groups, which is characteristic of other palladium and nickel complexes of phosphine. When chiral aminoalkylferrocenylphosphinenickel complexes are made to undergo this reaction, the corresponding optically active compounds are formed with a high stereoselectivity[262]. The same procedure has been used successfully for the asymmetric synthesis of terpenes[263]. It has also been shown recently that $(Ph_2PC_5H_4)_2FeNiCl_2$ is an effective catalyst of the reactions of t-alkyl Grignard reagents with bromostyrene[264], which results in the selective formation of $PhCH=CHCMe_3$. The application of nickel and cobalt compounds with polyfunctional aminophosphineferrocene ligands as catalysts of the isomerisation of alkyl groups[265] and prochiral allylamines[266] has been described. The initiating effect of the chelate complexes of ferrocenoylacetone in the polymerisation reactions of styrene and methyl methacrylate has also been described[267,268]. There are data concerning the catalytic activity of HMF in the thermolysis of $KClO_4$ [269] and as regulators of the combustion of rocket fuels[270]. The advantages of the application of salts of ferrocenesulphonic acid in rocket fuels compared with ferrocene have been noted[270]. It has been suggested that chromium complexes of ferrocenoylacetone be used as antistatic additives to petroleum products[4,48,221]. The application of the Fc–Li + Cp_2TiCl_2 mixture for the fixation of nitrogen[271], of the $TiCl_4$

complex of ferrocene in the photopolymerisation of epichlorohydrin[272], and of the salt $FeCp_2[Ni(S_2C_4F_6)_2]$ in dactyloscopy[20] has also been noted. The effectiveness of HMF in the synthesis of various ferrocene derivatives has been described in previous Sections.

The possibility of oxidising ferrocene to the cationic form and of carrying out the classical reactions of organic chemistry with the latter and the relatively ready availability of ferrocene derivatives permitted a successful development of synthetic studies designed to produce various heterometallic derivatives of ferrocene. A multiplicity of compounds of this type, containing virtually all transition metals, have been obtained. The data described in the review indicate the main pathways leading to the specific synthesis of HMF with specified structures and properties. The specific synthesis is facilitated when the classification of HMF proposed in this review and based on the characteristic features of the bond between the heterometal or its derivative and the ferrocene fragment is used, since such features determine the specific characteristics of the synthetic reactions of HMF of different classes. Because of this, definite possibilities arise in the planned synthesis of new HMF.

The successful development of synthetic studies created a basis for the practical application of HMF but hitherto only a few of them have found such applications. This is apparently because the majority of the compounds have been obtained in recent years and their properties have been inadequately investigated. The available data on HMF suggest that they will exhibit specific properties, particularly in catalysis, in various chemical reactions, and especially in the synthesis of ferrocene derivatives and optically active compounds which are otherwise difficult to obtain. However, at present it is still by no means always clear which characteristics of HMF determine the manifestation of particular useful practical properties of these compounds.

During the preparation of the review for the press, new studies on the synthesis, properties[273–287] and applications[288–293] of HMF were published.

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Bivalent Tin Analogues of Carbenes

V.I.Shiryaev and Y.F.Mironov

The structure and certain chemical and physiocochemical properties of bivalent tin compounds (stannylenes) are examined and the electronic, structural and chemical similarity between these compounds and carbenes and their analogues—bivalent compounds of Group IVB elements—is demonstrated. The possibilities of stannylenes in the synthesis of organotin (IV) compounds as well as complexes in which stannylenes are electron-donating ligands, like carbenes, are analysed. The bibliography includes 457 references.

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I. INTRODUCTION

During the last 15–20 years, the chemistry of bivalent tin compounds has developed rapidly; their structural and chemical similarity to compounds of other Group IVB elements in their lowest oxidation state—the bivalent compounds of carbon (carbenes)[1-5] and their closest analogues in the subgroup (silylenes, germylenes, and plumbylenes)[6-24]—is becoming increasingly evident.

Certain questions of the chemistry of tin(II) compounds have been reflected in monographs and reviews devoted mainly to the chemistry of quadrivalent tin[25-33]. The review by Donaldson[34], in which the structure and chemical properties of tin(II) compounds (mainly inorganic) were considered for the first time fairly fully (on the basis of the literature data up to 1966) as well as a series of reviews devoted to individual aspects of the chemistry of these compounds[9,18,35-38] merit special attention. For further information concerning the review literature and various problems of the synthesis, properties, and structure of tin(II) compounds, the reader is recommended to consult the Bibliographic Guide[39].

Numerous data indicating the chemical and structural similarity of carbenes and their analogues were first considered thoroughly in the review of Nefedov and Manakov[6] and later also other reviews[40-42], but they describe the chemistry of tin(II) compounds very briefly and incompletely. With the exception of relatively inaccessible publications in 1977 and 1978,[43,44] there has been hitherto no review analogous to those on silylenes and germylenes which would provide an adequate survey of studies demonstrating the structural and chemical similarity of tin(II) compounds to carbenes and their analogues. This review, which surveys studies published up to 1980, aims to fill this gap to some extent.

II. THE STRUCTURE AND PROPERTIES OF BIVALENT TIN COMPOUNDS

As a Group IVB element, tin has the outer electronic configuration ns^2np^2 in the ground state and, like its nearest neighbours in the subgroup (germanium and lead), can form stable compounds not only in the quadrivalent but also in the bivalent state. The formation of covalent inorganic and organic tin(II) compounds as well as organotin(II) compounds† can take place as a result of the employment of two unpaired p electrons (Fig.1).

Like carbenes and their analogues, in this case tin(II) compounds have the structure in the gas phase which can correspond in the one-electron approximation (i.e. when the fully occupied low-lying and vacant high-lying molecular orbitals are excluded from consideration) to the σ^2, σp, and p^2 configurations (Fig.2). The σp configuration can then be both singlet ($^1\sigma p$) and triplet ($^3\sigma p$), while the σ^2 and p^2 configurations are singlet.

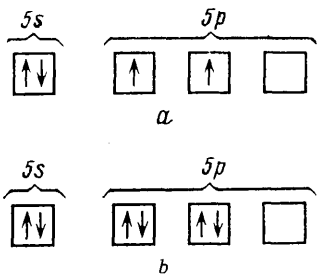


Figure 1. The distribution of electrons in the ground state: *a*) tin atom; *b*) SnX_2 molecule.

In the gas state at high temperatures, tin(II) dihalides are monomeric[45] and the study of their emission spectra under such conditions has shown that the SnX_2 molecules are non-linear[46]. The chemiluminescence emission spectra of SnX_2 in a flame[47] as well as the Raman spectra of the vapours of $SnCl_2$ [48,49] and other compounds of the type SnX_2 [50] at temperatures above 630 °C confirm the non-linearity of the structure of tin(II) dihalides under these conditions. Electron diffraction studies of the vapours of tin(II) dihalides established that the valence angle in their molecules is close to 95°.[50]

The results obtained agree with one another and also with infrared spectroscopic[51,52] and Mössbauer spectroscopic[53] data for tin(II) dihalides fixed in low-temperature inert matrices and make it possible to refine the values of the valence angles in the SnX_2 molecules (90–94°). Comparison of the bond angles and lengths in tin(II) dihalides and the dihalides of other Group IVB elements[9,40,41,50] shows that they are all isostructural and the closeness of the bond angles to 90° suggests that, like other carbene analogues,

† In contrast to organotin(II) compounds having at least one Sn–C bond, there is no direct bond between tin and carbon in organic compounds of tin(II).

stannylenes have a singlet ground state ($^1A_1$).[40,41] The singlet state of dihalogenostannylenes is confirmed by the fact that the energies of their orbitals (between −10 and −11.5 eV), determined from the ionisation potentials[54,55], are close to the energies of the σ orbitals of dihalogeno-derivatives of carbenes, silylenes, germylenes, and plumbylenes[40,41].

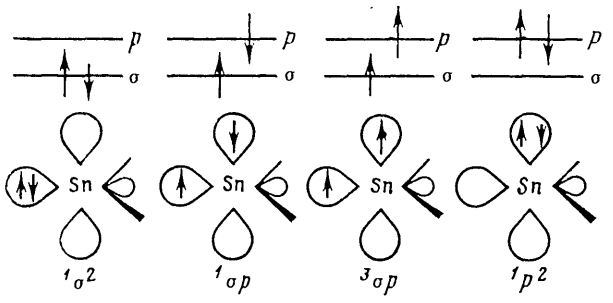


Figure 2. The structure of tin(II) compounds.

The direct determination of the energies of the *p* orbitals of stannylenes is impossible, but they can be estimated from the differences between the energies of the σ and *p* orbitals, which can be determined from the energy of the transition from the ground to the excited state ($^1A_1 \rightarrow {}^1B_1$). It was found that the energies of the *p* orbitals of dihalogeno-stannylenes (−6– −7 eV) are somewhat higher than the energies of *p* orbitals of carbenes but are very close to those of silylenes, germylenes, and plumbylenes. Thus the σ^2 configuration with a vacant *p* orbital makes the dominant contribution to the ground state of dihalogenostannylenes.

As in dihalogenostannylenes, in certain free stannylenes of other types in the gas phase and in the low-temperature matrices the tin orbitals are in a state close to sp^2. Thus spectroscopic investigations support a singlet ground state in a few diorganostannylenes[56] and stannylenes of the type $Sn(NR^1R^2)_2$.[57–59]

In a study of the phosphorescence observed in the GeO, GeS, SnO, and SnS molecules[60] isolated in low-temperature matrices, their lifetimes in the excited triplet states were calculated (3–100 μs).

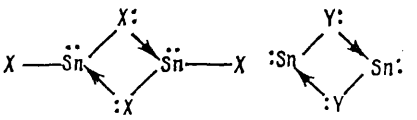


Figure 3. The structure of the dimers $(SnX_2)_2$ and $(SnY)_2$.

Mass-spectrometric studies of tin(II) halides and tin(II) monoxide[61,62] in the vapour phase revealed the presence, together with monomers, of the corresponding dimers, which consist, according to the spectroscopic studies of $(SnX_2)_2$ and $(SnO)_2$ molecules[52,53,63–66] as well as $(SnY)_2$ (Y = S or Se) [67] isolated in matrices at a low temperature, of four-membered rings formed as a result of the coordination interaction of the free electron pair of halogen, oxygen, sulphur or selenium with the vacant p orbital of the tin atom (Fig.3).

Structural and other physicochemical studies have shown that in the condensed (liquid or solid) phase many tin(II) compounds with electronegative substituents incorporating heteroatoms having unshared electron pairs are coordination polymers where the tin atoms employ in the hybridisation their own free *p* and *d* orbitals. Thus the X–Sn–X bond angles are somewhat less than 90° in crystalline anhydrous SnF_2,[68] $SnCl_2$,[69,70] $SnBr_2$,[71] and SnI_2 [72] and also in the mixed tin(II) halides[73,74], while their molecules form a coordination polycarbenoid layer structure (Fig.4), in which the free electron pair of the tin atom is involved in the hybridisation of the orbitals. The tetragonal tin monoxide $(SnO)_n$ [75] and tin(II) sulphide[69], selenide, and telluride[76] have similar structures.

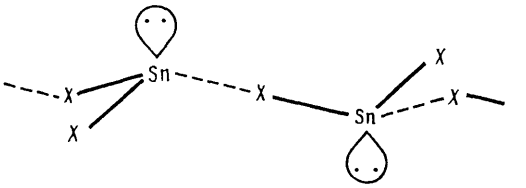


Figure 4. The layer structure of crystalline $(SnX_2)_n$.

The study of the Raman[77] and absorption[78] spectra of a melt of tin dichloride over a wide temperature range showed a gradual breakdown of the $(SnCl_2)_n$ chains with increase of the temperature of the melt. The weaker axial coordinate bonds begin to dissociate first and at a high temperature *in vacuo* free stannylenes can be formed in the gas phase[45,46,48–50]. The coordinate bonds in the polycarbenoid chains $(SnX_2)_n$ can break down also under the influence of electron-donating solvents (Solv) which results in the formation of discrete carbenoid complexes $Solv.SnX_2$, in which the tin atom is an acceptor of the electron pair of the solvent. The synthesis and properties of numerous complexes of this kind have been described in reviews[32,34]. It is of interest to note that the geometry of carbene-like molecules in such complexes differs little from the geometry of the free stannylenes, as shown by the similarity by the geometries of dichlorostannylenes and its complex with dioxan[79].

Organic compounds of tin(II) consists of a large group of compounds in which the organic moieties are linked to the tin atom via a heteroatom (oxygen, nitrogen, sulphur, phosphorus, and others). It has been established mass-spectrometrically that some of these [for example, $Sn(OCOAr)_2$,[80] bis(diketonato)tin(II),[81] and tin(II) amides[57,58]] are monomeric in the gas phase and also in solution. The majority of organic compounds of tin(II) having electron-donating heteroatoms are coordination intra- or inter-molecular complexes in the liquid and crystalline state. The most common types of compounds of this kind are cyclic[82–85] and linear[86–90] tin(II) alkoxides as well as acyloxy-derivatives of tin(II).[91–94]

Chelates with Sn–O bonds, such as bis(1,3-diketonato)-tin(II),[81,95–97] tin tropolonates[98], and many other tin(II) chelates[97,99–101] constitute a large group of organic compounds of tin(II). Their crystal structures have not been established in most cases, but the available X-ray diffraction data for solid bis(benzoylacetonato)tin(II) [101] and bis(1,3-diphenylpropane-1,3-dionato)tin(II) [102] suggest that their

ligands are bidentate and that the tin atom is an sp^3d hybrid (Fig.5*a*). It is believed[95,103] that the tin atom in 1,3-diketonatotin(II) halides is in the sp^3 configuration (Fig.5*b*). The tin atom in the monomeric product $Sn(OCH_2CH_2)_2NCH_3$ is evidently in the same state (Fig.5*c*).[104]

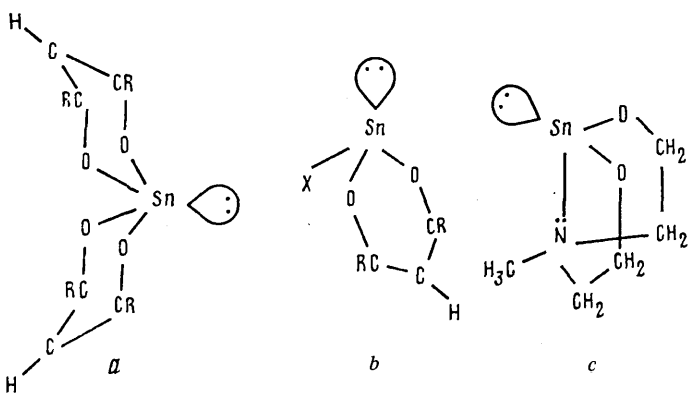


Figure 5. The structures of certain organic compounds of tin(II): *a*) bis (1,3-diketonato)tin(II); *b*) 1,3-diketonatotin(II) halides; *c*) $Sn(OCH_2CH_2)_2NCH_3$.

The crystal structure of bis(*O*-methyl dithiocarbonato)-tin(II),[105] bis(diethyldithiocarbamato)tin(II),[106] and diazasilastannetidines[107] are in principle analogous to the structures presented above. The structures of other organic compounds of tin(II), containing the Sn–N,[104,108-111] Sn–P,[112] Sn–As,[113] and certain other bonds[100,103,114] have not been established exactly although it has been suggested that the dimers of some of them, which exist in solutions, have structures analogous to those of the tin(II) dihalide dimers (Fig.3).

Little is so far known about the structures of organotin(II) compounds. The reason for this is in the first place that only few compounds of the type R_2Sn: (the first was obtained as early as 1852 [115]) can retain the tin atom in the bivalent state for a long time. In the vast majority of cases, regardless of the methods of their synthesis, diorganostannylenes polymerise very readily (see Section III). Certain organotin(II) compounds containing specific groups, which prevent the polymerisation of diorganostannylenes to the corresponding polystannanes, constitute an exception. Such compounds include dicyclopentadienyltin(II) [116] and bis-(methylcyclopentadienyl)tin(II),[117] which contain the cyclopentadienyl groups (Cp)—carriers of a closed π-electron system. Gas-phase electron diffraction studies established that the Cp^2Sn molecule has an angular sandwich structure[118] (Fig.6*a*).

Although dicyclopentadienyltin(II) is monomeric in the gas phase and in benzene solution, in the solid state it is a coordination polymer in which the cyclopentadienyl rings form a kind of bridges between the tin atoms (Fig.6*b*). In solid cyclopentadienyltin(II) chloride the coordination polymer is formed as a result of Cl...Sn coordinate bonds (Fig.6*c*). Other more exotic examples of organostannylenes are presented in Fig.7.[119-122]

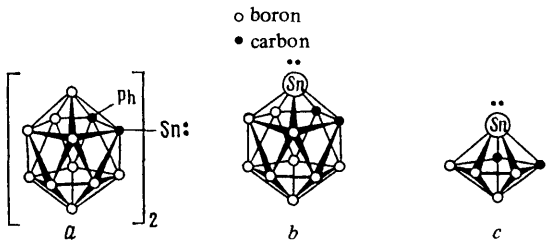


Figure 7. Some examples of organostannylenes: *a*) bis[2-phenyl-1,2-dicarba-*closo*-dodecaboran(12)-1-yl tin(II); *b*) 3-stanna-1,2-dicarba-*closo*-dodecaborane(11); *c*) small tin(II)-containing metallocarbaboranes.

The synthesis of the first stable dialkylstannylene containing two bis(trimethylsilyl)methyl groups, namely $[(Me_3Si_2)CH]_2Sn$:, was reported in 1973.[123] Its structure in the gas phase was not investigated but it was shown mass-spectrometrically that it exists in a free state: it is monomeric in solution and spectroscopic data indicate a singlet

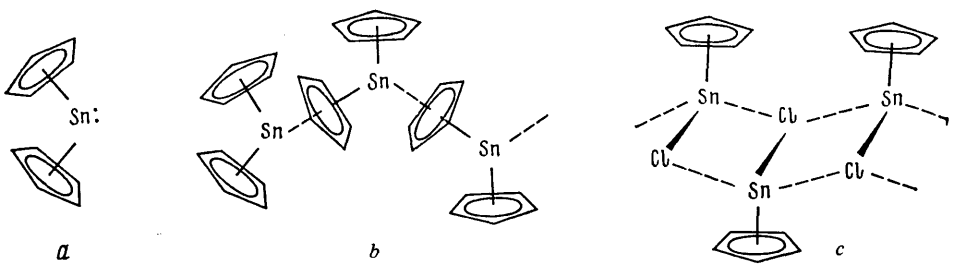


Figure 6. The structure of cyclopentadienyl derivatives of tin(II): *a*) Cp_2Sn in the gas phase; *b*) Cp_2Sn in the solid state; *c*) CpSnCl in the solid state.

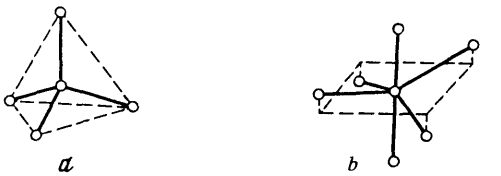
ground state of the molecule[56]. This has been confirmed by the study of the crystal structure of the complex $\{Cr(CO)_5 . Sn[CH(SiMe_3)_2]_2\}$ in which the valence angle of the diorganostannylene is close to 98°.[124] According to X-ray diffraction data[125], in the solid state $Sn[CH(SiMe_3)_2]_2$ is a dimer, whose curved bonds are formed as a result of the mutual overlap of the free electron pair of the tin atoms with their unoccupied *p* orbitals[56]. The angle between the C–Sn–C bonds then increase to 112°.

Numerous other compounds, which were believed for a long time to have been diorganostannylenes, proved to be polystannanes with a quadrivalent tin atom. Valuable information, which makes it possible to establish the valence state of the tin atom, is provided by Mössbauer or γ-resonance spectroscopy. The isomer shifts (*IS*) in the Mössbauer spectra of the majority of tin(II) compounds are in the range 3–4 mm s^{-1} (here and henceforth the values of *IS* are quoted relative to SnO_2), which indicates an appreciable *s*-electron density at the tin nuclei. This is a consequence of an appreciable *s* character of the orbital occupied by the free electron pair. When the environment of the resonating nuclei is non-spherical, usually two peaks are observed in the Mössbauer spectrum (quadrupole splitting); on the other hand, when the *s*-electron cloud is fully spherical, there is no quadrupole splitting. Information about the Mössbauer spectroscopy of tin(II) compounds can be found in a number of publications[53,126–129].

The diorganostannylene $[(Me_3Si)_2CH]_2Sn$ has a small isomer shift (*IS* = 2.16 mm s^{-1}) compared with other organotin(II) compounds[123,130], which is consistent with the difference between its structure and those of other diorganostannylenes—Cp_2Sn, CpSnCl, and CpSnBr (Fig.6)—in which the isomer shift (3.76 mm s^{-1},[131] 3.90 mm s^{-1}, and 3.69 mm s^{-1} [103,132] respectively) is only slightly smaller than for $SnCl_2$ (4.07 mm s^{-1}).[133] In solid $[(Me_3Si)_2CH]_2Sn$ the *s* electrons are involved in the formation of a dimer with weak Sn–Sn bonds (see Section III, subsection 1), while cyclopentadienyltin(II) compounds have no Sn–Sn bonds and are characteristic examples of tin(II) compounds with a non-bonding electron pair at each tin atom. Compounds of the type $(R_2Sn)_n$ (R = Bu, Ph, etc.) are polymeric or cyclic with a strong Sn–Sn interaction and their isomer shift (0.72 to 1.55 mm s^{-1}) [131,134] correspond to the quadrivalent state of the tin atom. Their structures have been demonstrated by chemical[25,26,135] and spectroscopic[136–138] methods and also by X-ray diffraction[139].

It is known that under certain conditions (in the vapour phase at the high temperature) carbon, silicon, and germanium form atomic species, which manifest carbene-like properties[4]. As will be shown below, tin in the vapour phase also exhibits similar properties. Metallic tin exists in two allotropic modifications: the α-form (grey tin) and the β-form (white tin). β-Tin is converted into the α-form fairly readily at +18 °C and below, particularly on contact with even very small amounts of α-tin. The shift *IS* in the Mössbauer spectrum is 2.56 mm s^{-1} for β-tin [140] (*IS* = 2.06 mm s^{-1} for α-tin [141]), i.e. it adjoins the region in which the values for tin(II) compounds are located.

In contrast to the tetrahedral configuration of α-tin (Fig.8*a*), in the β-form (Fig.8*b*) each tin atom is in a somewhat distorted octahedral environment characteristic of tin(II) compounds. Since the distance between the nearest tin atoms in the β-form is somewhat greater than in the α-form, the Sn–Sn bonds in β-tin should be weaker. The octahedral environment in β-tin probably entails the involvement of the free electron pair in hybridisation and the occurrence of donor–acceptors interactions (although these may be weak) between the tin atoms. Consequently Sn(II) binding evidently occurs in β-tin and the latter can be regarded as a carbene-like layer polymer with donor–acceptor bonds between the layers. Chemical confirmation of this is provided by the formation of tin(II) dihalides from β-tin and hydrogen halides (see Section III). Tin(IV) tetrahalides are formed from α-tin under analogous conditions[32]. It is noteworthy that atomic tin, fixed in a nitrogen matrix, has *IS* = 3.23 mm s^{-1} in the Mössbauer spectrum[142] and therefore consists of the free stannylene—more precisely the bistannylene $\dot{S}n$.



a *b*

Figure 8. Configurations of α-tin (*a*) and β-tin (*b*).

III. REACTIONS OF STANNYLENES LEADING TO THE FORMATION OF QUADRIVALENT TIN COMPOUNDS

A consequence of the electronic and structural similarity of stannylenes to other carbene-like molecules of Group IVB elements with covalence unsaturation is the ability to form new chemical bonds. The presence of the stereochemically active free electron pair enables stannylenes, like carbenes, silylenes, and germylenes, to polymerise, to become inserted in single bonds, to add to carbon–carbon double bonds, etc. and also to form carbenoid complexes in which stannylenes behave as donors of an electron pair. The high reactivity of carbene-like molecules is determined mainly by the electrophilicity of the vacant *p* orbital, which decreases appreciably from carbenes to silylenes, but changes little in the series of germylenes, stannylenes, and plumbylenes[40,41].

1. Dimerisation and Polymerisation of Stannylenes

One of the main characteristic properties of carbenes, which follows from their covalence unsaturation, is the ability to form one (sp^2) or two (sp^3) new covalent bonds. The carbene-like compounds of Group IVB elements, including stannylenes, are not exceptional in this respect although the formation of a single new covalent sp^2 is energetically less favourable for these elements[40,41]. The possibility of the existence of the dimers of certain organic compounds of tin(II), namely $(R_2P)_2Sn{=}Sn(PR_2)_2$ and $(Me_2N)_2Sn{=}Sn(NMe_2)_2$, has been postulated by some workers[143,144], while the dimer $\{[(Me_3Si)_2CH]_2Sn\}_2$, which has been isolated and characterised in the crystalline state, has, as mentioned above, a weak Sn–Sn bond which readily dissociates on dissolution in benzene[125].

Presumably the absence in the vast majority of instances of "olefinic" stannylene dimers from the reaction products can be explained by their extremely high reactivity and especially their tendency to polymerise[25,26,28,30,31,33,145,146]:

$$n/2\,[R_2Sn{=}SnR_2] \rightarrow n/2\,[R_2\dot{S}n{-}\dot{S}nR_2] \rightarrow (R_2Sn)_n .$$

The reduced ability to polymerise of a few of the diorganostannylenes presented in Fig.7 can be accounted for primarily by steric factors due to the presence of bulky substituents. Steric factors are not the only cause of the decrease

of the ability of stannylenes to dimerise and polymerise. Thus the reduced capacity for polymerisation of Cp_2Sn molecules agrees with the postulated filling of the unoccupied *p* orbital of the tin atom by the π electrons of the cyclopentadienyl ring (Fig. 6*b*). The polymerisation of Cp_2Sn becomes possible in the presence of dimethylformamide (DMF).[131] Similarly the "filling" of the unoccupied *p* orbital of the tin atom by the free electron pair of a halogen, oxygen, or sulphur atom or another donor of an electron pair in inorganic and organic compounds of tin(II) lowers their ability to polymerise with formation of Sn–Sn bonds. An instance of the copolymerisation of $SnCl_2$ with methylene, generated from CH_2N_2, is known[147]:

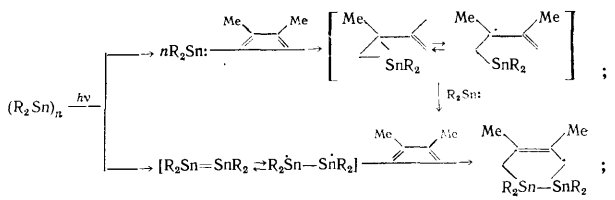
$$:SnCl_2 + :CH_2 \rightarrow [H_2C{=}SnCl_2] \rightarrow [-SnCl_2-CH_2-SnCl_2-CH_2-]_n \ .$$

2. The Reactions of Stannylenes with Unsaturated Compounds

The main and preparatively most interesting reaction of carbene is that with the multiple bonds of unsaturated compounds leading to the formation of cyclopropane or cyclopropene derivatives[1–6]. When carbene analogues, derivatives of Group IVB elements, react with olefins, the products of the further reactions of the corresponding heterocyclopropanes rather than the heterocyclopropanes themselves are isolated.

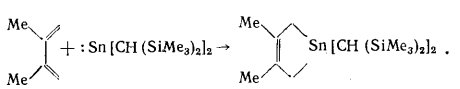
The polymer $(-CF_2-CF_2-SnPh_2-)_n$, the product of the formal addition of diphenylstannylene to the C=C bond, has been obtained in the photolysis of $(Ph_2Sn)_n$ in the presence of tetrafluoroethylene[148].

The photolysis of cyclic polystannanes $(R_2Sn)_n$ in the presence of 2,3-dimethylbutadiene yielded additional products containing two tin atoms in the ring[149]. The formation of these products can be represented as a result of the 1,4-addition of the biradical $R_2\dot{S}n-\dot{S}nR_2$ or the consecutive addition of the stannylenes R_2Sn: to the diene:



R = Me, n-Bu .

The 1,4-cycloaddition of $[(Me_3Si)_2CH]_2Sn$ to 2,3-dimethylbutadiene takes place readily (in hexane at room temperature) and this is perhaps the only example in which it has been shown unambiguously that free diorganostannylenes participate in the formation of the addition product[150]:



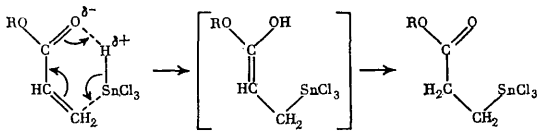
Conflicting data have been obtained in reactions of tin(II) dihalides[151,152], organic compounds of tin(II),[153] and organotin(II) compounds[146] with acetylenedicarboxylate esters: in some cases the formation of the corresponding addition products has been reported, while in others it is claimed that complexes are formed whose Mössbauer spectra contain a doublet in the region characteristic of bivalent tin, which corresponds to a structure with simple donor–acceptor interaction. Analogous complexes are probably formed in reactions of stannylenes with diethyl diazodicarboxylate[103,152] and with tetracyanoethylene[154–156].

It has been established recently that trichlorostannane etherate (see subsection 4 below), which has a structure analogous to trichlorogermane etherate[157–159], interacts with unsaturated compounds having a carbonyl group in the α-position relative to the carbon–carbon bond (acrylates, crotonates, acrylic and methacrylic acids, acryloyl chloride, phorone and others), giving rise to high yields of hydrostannylation products[159–163]:

$$RO-\overset{\overset{O}{\|}}{C}-CH{=}CH_2 + HSnCl_3 \cdot 2Et_2O \rightarrow RO-\overset{\overset{O}{\|}}{C}-CH_2CH_2SnCl_3 \ .$$

The etherates of $HSnX_3$ react similarly with the methyl esters of acetylenecarboxylic acids $RC{\equiv}CCO_2CH_3$ (R = H, Me, Ph, or $COOCH_3$), forming the corresponding 1,4-addition products $Cl_3SnCR{=}CHCO_2CH_3$ and the products of their further reactions[164].

The mechanism of these reactions is not altogether clear. The ionic 1,4-addition of $HSnCl_3$ is believed to be the most probable[159,161–163]:



The analogous reaction of the etherates of $HSnX_3$ with unsaturated compounds of the type of acrylonitrile[165], in which the carbon–carbon double bond is activated by conjugation with a C≡N bond, has also been described.

3. The Insertion of Stannylenes in Single Bonds

The insertion in single bonds is a general reaction of those carbenes[1–5] and their analogues[6–24,40,41] although the latter should exhibit a greater selectivity in this process than carbenes, whose electrophilicity is higher. Instances of the insertion of stannylenes in various single bonds are known: C–X, M–X, C–M, M–M, S–S, etc.

(a) The insertion of stannylenes in a carbon–halogen bond. This reaction discovered by Pfeiffer and Heller almost 100 years ago[166] is of great practical importance, since it makes it possible to obtain in a single stage compounds which are usually difficult to synthesise:

$$R-X + SnY_2 \rightarrow RSnY_2X \ .$$

The reactivity of alkyl halides in these reactions decreases appreciably in the sequence RI > RBr > RCl, so that different catalysts are used to achieve a successful reaction with bromides and even more so, chlorides: amines[167], phosphines[168] (and their onium salts), bivalent sulphur and selenium compounds[169], salts of various Group I–III metals[170–173], and tervalent antimony compounds[174,175]. In conformity with the influence of steric factors, the yield of reaction products decreases with increase of the number of carbon atoms in the alkyl group R.[175]

This reaction has been used successfully to develop an industrial method of synthesis of $MeSnCl_3$ [172,176] and also for the development of preparative methods of synthesis of carbofunctional trihalogenostannanes which are difficult to obtain, for example[175,177–179,180–182]:

$$X(CH_2)_nX + SnX_2 \rightarrow X(CH_2)_nSnX_3 \ ;$$

X = Cl, Br; n = 1, 3, 4, 5, 6 ;

$$Y_nMe_{3-n}SiCH_2Cl + SnCl_2 \rightarrow Y_nMe_{3-n}SiCH_2SnCl_3 \ ;$$

Y = alkyl, aryl, cyclopropyl, F, Cl, MeO, EtO, RCOO; n = 0–3 ;

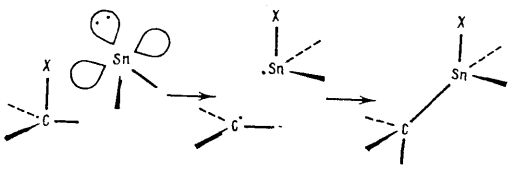
$$R_3SiCH_2Cl + SnO \rightarrow [R_3SiCH_2Sn(O)Cl]_4 + R_3SiCH_2SnCl_3 + (R_3SiCH_2)_2SnCl_2 \ .$$

Different diorganostannylenes R_2Sn, obtained by the thermal, photolytic, or some other method, are also inserted in the carbon–halogen bonds of organohalogen compounds[103,146,149,150,153,184–194] and their reactivity is so high that, for example, $[(Me_3Si)_2CH]_2Sn$ is inserted even in the C_{ar}–Cl bonds of chlorobenzene[184].

The reactivity of organic compounds of tin(II) without the C–Sn bond is somewhat lower than that of diorganostannylenes; nevertheless the products of the insertion of various tin(II) chelates[95,98,103,153,195,196] and also $[(Me_3Si)_2N]_2Sn$ [184,185] and $[(CO)_5M]_2Sn$ (M = Cr, Mo, or W) [197] in the C–I bond in alkyl iodides and in the activated C–halogen bonds of organobromine or organochlorine compounds have been obtained in high yields.

Finally, the reactions of the anions $:SnX_3^-$ and $:Sn(OH)_3^-$, having stereochemically active free electron pairs, with organic halides RX, leading to the formation of the product of the formal insertion in the C–X bond, have been described[198–201]. It has been suggested that the insertion of stannylenes in the C–X single bond in organic halides constitutes the basis of a direct synthesis of organotin halides[202–205]. It has been established that free (in the vapour phase) tin atoms readily react with alkyl halides to form the intermediate [RSnX] (R = Me, Et, or Bu; X = Br or I).[206] It has been shown for the intermediate [BuSnBr], isolated at a low temperature, that these alkylhalogenostannylenes are highly reactive with respect to various reagents and are particularly readily inserted in the C–halogen bonds in alkyl halides to form R_2SnX_2—the desired product of the direct synthesis.

The mechanism of the insertion of stannylenes in the C–halogen bond is not altogether clear[207–209]. Bearing in mind the fact that stannylenes are isostructural with singlet carbenes, silylenes, and germylenes, a common mechanism may be expected for the insertion of these species in single bonds[40,41,43], according to which the electrophilic unoccupied *p* orbital of the carbene or its analogue attacks the corresponding bond. Next the reactive molecules approach one another, which is accompanied by the migration of the halogen to the tin atom and the recombination of the resulting close radical pair.



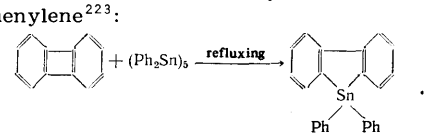
It may be that in the catalytic reactions of SnX_2 or $(R_2Sn)_n$ with R'X the electron-donating catalyst molecules promote the dissociation of the polymer chain of the polystannylene and the formation in solution of discrete stannylene molecules. In some communications the insertion of stannylenes in C–halogen bonds is regarded as a radical-chain process[185,194].

(b) The insertion of stannylene in the C–M, C–C, M–M, and M–H bonds. Like carbenes, diorganostannylenes R_2Sn are readily inserted in the C–Li, C–Na,[210] and C–Mg[211] bonds with formation of compounds of the type R_3SnM (M = Li, Na, or MgX). The appearance of branches in the polymer chain of $(R_2Sn)_n$ [25,26,28,191] and the formation of $(R_3Sn)_3SnLi$ when an attempt is made to isolate R_3SnLi from solution[212,213] can probably be explained by the insertion of diorganostannylenes in the C–Sn bond. This is confirmed by the formation of $Me_3SnSnBu_2Me$ in the reaction of Bu_2Sn with Me_4Sn.[149] One cannot rule out the possibility that the familiar reaction involving the displacement of mercury from its dialkyl and particularly diaryl derivatives by tin(II) dihalides and diorganostannylenes also proceed via the initial insertion of stannylenes in the C–Hg bond:[214–218]

$$R{-}Hg{-}R + SnY_2 \rightarrow [R{-}Hg{-}SnY_2{-}R] \xrightarrow{-HgY_2} R_2SnY_2\ ;$$
Y = halogen, alkyl, or aryl.

Stannylenes are inserted just as readily in carbon–transition metal bonds. The insertion of $Sn(NR_2)_2$ [219] and SnX_2 (X = Cl or Br) [220–222] in the Fe–C bond and also of $[(Me_3Si)_2CH]_2Sn$ [150] in the Mo–C and Fe–C bonds has been described.

So far only one example of the insertion of stannylene in a carbon–carbon bond is known, namely in the strained C–C bond of biphenylene[223]:



Like the carbonoid molecules of other Group IVB elements, paricularly germylenes[20–22], stannylenes are readily inserted in metal–metal bonds. In particular, the insertion of diorganostannylenes in the Sn–Na [6,224,225] and Sn–Sn [149,188,192,226–228] bonds and also the insertion of $SnCl_2$ in the B–Hg bond[229] are known. However, this reaction is represented most widely by instances of the insertion of stannylenes in the M–M bonds of dinuclear compounds of transition metals [L is a ligand of the type CO, Cp, PR_3, $P(OR)_3$, etc.]:

$$L_xM{-}ML_x + SnY_2 \rightarrow L_xM{-}SnY_2{-}ML_x\ .$$

Examples of the insertion of stannylenes in the Fe–Fe,[230–232] Ni–Ni,[233] Co–Co,[118,233–239] Cr–Cr, Mo–Mo, W–W,[240] Mn–Mn, and Re–Re [241–243] bonds have been described. The synthesis by this method of tin-containing carbonyl complexes of iron, cobalt, rhenium, and rhodium fixed on a carrier has been reported[244]. Mössbauer spectroscopic data are available for certain products of insertion in M–M bonds, showing that the tin atom in such products is in the quadrivalent state of oxidation (*IS* = 1.27–1.99 mm s^{-1}).[231–237,245–247] It is believed [248] that the formation of $Sn[Co(CO)_4]_4$ from metallic tin and $Co_2(CO)_8$ also involves the insertion in the Co–Co bond initially of the Sn atom and then of the intermediate stannylene $[Co(CO)_4]_2Sn$:.

A few examples indicating the ability of stannylenes to be inserted in the Sn–H [6,149] and Mo–H [124,150,249] bonds are also known.

(c) Insertion of stannylenes in M–X bonds. There are very few examples of the insertion of stannylenes in a non-transition metal–halogen bond. In particular, reactions involving the insertion of diorganostannylenes in the Sn–Cl bond[226,228] and also of metallic tin[217], dihalogenostannylenes[250], and di(permethylcyclopentadienyl)tin(II) [251] in the Hg–X bond have been described. The reaction involving the insertion of stannylenes in a transition metal–halogen bond is more general. Examples of the insertion of dihalogenostannylenes in the Fe–Hal,[130,150,231,232,246,252–256] Cr–Hal, Mo–Hal, W–Hal,[40,257] Co–Hal,[258,259] Rh–Cl,[124,140] Pd–Cl,[260–262] Pt–Cl,[255,263–265] Ir–Cl,[140,255,266] Mn–Hal,[266] Ni–Cl,[267] and Ru–Hal [255,268,269] bonds and also of $[(Me_3Si)_2CH]_2Sn$ in the Pt–Cl,[130] Fe–Cl,[130,150] and Rh–Cl [124] bonds are now known.

The reactions are usually carried out in polar or non-polar solvents at room temperature or with slight heating; sometimes the process is initiated photolytically. The isomer shifts *IS* in the Mössbauer spectra of the products of the insertion of stannylenes in the M–X bonds are 1.54–2.02 mm s^{-1},[130,140,150,231,246,253,256,258,259,270] which corresponds to the quadrivalent oxidation state of the tin atoms. However,

in certain similar instances the isomeric shift for the formal products of the insertion of stannylenes in a transition metal–halogen bond are in the intermediate range or even in the range characteristic of bivalent tin. Such products, containing discrete SnX_3^- anions as electron-donating ligands, are formed via an ionic mechanism and are discussed below (in Section IV).

(d) The insertion of stannylenes in the S–S bonds of disulphides, the O–O bonds of peroxides, and certain other bonds. Different types of stannylenes are extremely readily inserted in the S–S bonds of diorganodisulphides:

$$Y_2Sn + RS{-}SR \rightarrow RS{-}SnY_2{-}SR ,$$

where Y = Me, Bu, Ph,[149,253] Cp, OMe, SPh, chelate[103,153], oxinate (Ox),[271] or halogen[152,272,273] and R = alkyl, phenyl, Br, Py, or (iso-Pro)$_2$P(S).

The insertion of tin(II) dihalides[152], diarylstannylenes[253], dialkylstannylenes[149,274,275], and tin(II) oxinates[271] in the O–O bonds of organic peroxides ROOR [R = alkyl or C(O)Ph] takes place just as readily, sometimes exothermically.

Examples of the insertion of dihalogenostannylenes in the P–O–P bond in diethylphosphoric and diphenylphosphinic acid anhydrides[276] and also in the N–Cl bond of *N,N*-dichloro- or *N*-chloro-*N*-methyldialkylphosphoramides[277] and the *N,N*-dichloramides of arenesulphonic acids[278] are known.

4. Reactions of Stannylenes with Oxygen, Sulphur, Phosphorus, Halogens, Hydrogen Halides, and Other Similar Compounds

One of the first reactions of diorganostannylenes discovered is their oxidation by atmospheric oxygen[25,26,31,33,150,225]:

$$R_2Sn + O_2 \rightarrow R_2SnO .$$

Organohalogenostannylenes RSnX [206] and organic compounds of tin(II) [81,97,279] are also readily oxidised in air. The capacities of inorganic tin(II) compounds for oxidation are different: tin(II) monoxide is oxidised in air only on heating[32]; tin(II) sulphate $SnSO_4$ is very resistant to oxidation[34]; solid tin(II) halides are slowly oxidised in air but in solutions the reaction is greatly accelerated[152]. In a study of the products of the reaction of atomic tin with oxygen in the vapour phase by the matrix isolation method, it was shown that the initial step in the formation of the main products (SnO_2, SnO, Sn_2O_2, Sn_3O_3, etc.) is the insertion of atomic tin in the O–O bond of the O_2 molecule[280].

Stannylenes react analogously with sulphur, forming the corresponding sulphides $(R_2SnS)_x$.[253,281–283] Diorganostannylenes react just as readily with white phosphorus[284,285] and tellurium[286] forming the corresponding insertion products $(Me_2Sn)_nE_m$ (E = P or Te; n = 3, 5, or 6; m = 2, 3, or 4).

When stannylenes react with halogens, a wide variety of halogenostannanes are formed very readily[6,98,99,103,150,153,186,206,251,271,281,287,288] (Y = halogen, alkyl, aryl, chelate, etc.):

$$Y_2Sn + X_2 \rightarrow Y_2SnX_2 .$$

Free diorganostannylenes react readily with hydrogen halides:

$$R_2Sn + HX \rightarrow R_2Sn(H)X .$$

where R = $(Me_3Si)_2CH$ [150] or t-Bu [289] and X = F or Cl.

On the other hand, protolytically unstable stannylenes undergo various reactions under the influence of hydrogen halides. Thus the cyclopentadienyl groups in Cp_2Sn are readily split off under the influence of HX to form CpSnX or SnX_2,[103,132] while the P–Sn bond in $(t\text{-Bu})_2P{-}Sn{-}Cl$ dissociates on treatment with HCl and $[(t\text{-Bu})_2\overset{+}{P}H_2]SnCl_3$ is formed[290].

In contrast to the analogous carbon, silicon, and germanium compounds, trihalogenostannanes $HSnX_3$, formed when SnX_2 reacts with dry hydrogen halides, are unstable[157]. However, in ethereal solution the $HSnX_3$ are stabilised as a result of the formation of relatively stable etherates $[Et_2O \rightarrow H...OEt_2]^+ . SnX_3^-$,[158] for which the more complex structure $H_nSnX_{2+n} . mEt_2O$ (m/n = 1.1–1.5) has been postulated[159]. The aminates of trihalogenostannanes $[R_3NH]^+SnX_3^-$ proved to be more stable[291,292].

Evidently the formation of SnX_3 from metallic β-tin and HX can also be regarded as a carbenoid reaction, although the formation of the extremely unstable intermediates [HSnX] and $[H_2SnX_2]$ still awaits confirmation:

$$\beta\text{-}Sn + HX \rightarrow [HSnX] \xrightarrow{HX} [H_2SnX_2] \xrightarrow{-H_2} SnX_2 .$$

IV. STANNYLENES AS ELECTRON-DONATING LIGANDS IN COMPLEXES

One of the characteristic properties of carbenes and their analogues is their ability to form complexes with various compounds of non-transition and transition metals[9,36,42,293–299]. By virtue of the presence of the σ orbital, which is a carrier of a nucleophilic free electron pair, stannylenes can also play the role of electron-donating ligands in complexes where the tin atom is in the lowest oxidation state. In connection with the increased interest in complexes of carbenes and their analogues, there has been a recent appreciable increase of the number of publications on the corresponding complexes of tin(II) compounds[18,33,34,36–38,42,44,300–308].

Treatment of tin(II) dihalides with an excess of organolithium, organosodium, organomagnesium, or organozinc compounds is known to result in the formation of the corresponding compounds of the type R_3SnM:[33]

$$Y_2Sn: + 2R{-}M \rightarrow R_2Sn: \xrightarrow{R-M} R_3SnM ;$$
$$M = Li, Na, MgX, ZnX .$$

As early as 1952, it was suggested that Rh_3SnLi is 20% dissociated in solution[309]:

$$Ph_3SnLi \rightleftarrows Ph_2Sn: + PhLi .$$

Later equilibrium between R_3SnLi, R_2Sn:, and RLi,[310,311] and also in the analogous reactions involving magnesium [312] and zinc [313,314] compounds, possibly with participation of stannylene–salt complexes of the type $R_2Sn.MR$, was frequently confirmed chemically, although Mössbauer spectroscopic data have shown that the values of *IS* in such cases correspond, with rare exceptions[315], to the quadrivalent state of the tin atom[211,313].

The possibility of the existence of such carbene-salt complexes has been postulated in the mechanism of Simmons–Smith reactions[315–318] and also in the explanation of numerous data concerning the appreciable influence of alkali metal salts present in the reaction medium on the properties of independently generated carbenes (the salt effect).[4,42,299,319,320]

In their reactions with stronger electron pair acceptors such as the trihalides of Group III elements, stannylenes form the stable complexes $Y_2Sn.MX_3$ [M = B or Al; Y = Cp, MeCp, $(Me_3Si)_2CH$, halogen, or chelate].[98,150,204,321–323] In a number of instances such complexes are formed as a result of the displacement of weaker ligands from their complexes with MX_3:[98,204,322,323]

$$Y_2Sn: + BX_3{\cdot}OEt_2 \rightarrow Y_2Sn{\cdot}BX_3 + Et_2O .$$

The Mössbauer parameters of these complexes (*IS* = 3.71 to 3.83 mm s^{-1}) [98,204,323] correspond to the bivalent state of the tin contained in them. The possibility of the formation

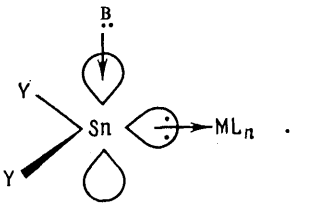
of the ionic complexes $[CpSn]^+MX_4^-$ or the bridged complexes $CpSn-X-MX_3$, in which there is no Sn–M σ-bond, has been discussed for organohalogenostannylenes of the type CpSnX in reactions with MX_3 (M = B or Al).[323–327]

As in carbene chemistry[42,293–299], complexes of stannylenes with various transition metal compounds are the most stable and have been investigated more than others. One of the main reactions involved in the synthesis of complexes of this kind is the displacement (photolytic or thermal) by stannylenes of other ligands, for example, carbon monoxide molecules, from transition metal carbonyls:

$$Y_2Sn: + LM(CO)_x \rightarrow CO + Y_2Sn\cdot M(CO)_{x-1}\cdot L \ ;$$
$$M = Fe, Cr, Mo, W, Mn;\ L = CO, Cp, MeCp, PhCN \ .$$

This reaction is common to different types of stannylenes—diorganostannylenes[38,123,124,150,328,329], organic compounds of tin(II) such as tin(II) chelates[330–332], $Sn(NMe_2)_2$,[144] $Sn[N(SiMe_3)_2]_2$,[37] $Me_2Si\begin{matrix}NR\\ \diagup\ \diagdown\\ NR\end{matrix}Sn$,[283] and 1,2,3-$SnC_2B_4H_4Me_2$,[122] as well as inorganic tin(II) compounds, in particular dihalogenostannylenes[331,333–336]. The more electrophilic ligand $[(Me_3Si)_2CH]_2Sn$ displaces norbornadiene ligands[124,150], Ph_3P,[124] and Et_3P [124,150] from transition metal complexes.

In some cases stannylene complexes are stabilised by the additional coordination interaction of the tin atom with the electron pair of a base B:[144,334,335]



Similar complexes are known also for silylenes and germylenes, where stabilisation as a result of coordination to a base B̈ evidently constitutes an essential condition for their stability[42,337–342]. An instance of a carbene complex with additional stabilisation by a base is also known, namely the complex $(CO)_5W.CPh_2.PMe_3$.[343]

Complexes of stannylenes stabilised by a base can also be obtained by the cleavage of complexes whose structure is based on the four-membered ring M_2Sn_2.[144,328,344–348] These complexes are readily cleaved by bases B̈ and the ability of the latter to split the Sn–M bond in the four-membered ring M_2Sn_2 decreases in the sequence[346,348] pyridine > dimethyl sulphoxide (DMSO) > acetone > tetrahydrofuran (THF) > diethyl ether. Weak bases in such complexes can be displaced by stronger bases:[349]

$$(CO)_5W\cdot SnCl_2\cdot THF + (Me_3C)_3P \rightarrow (CO)_5W\cdot SnCl_2\cdot P(CMe_3)_3 + THF \ .$$

The additional coordination interaction with the base B makes the stannylenes more nucleophilic and stabilises the stannylene complex to such an extent that various reactions involving the substitution of chlorine atoms in dichlorostannylene complexes become possible[197,350–352]:

$$(CO)_5M\cdot SnCl_2\cdot THF + Me_3Si{-}X \rightarrow (CO)_5M\cdot Sn\begin{matrix}X\\ \diagup\\ \diagdown\\ Cl\end{matrix} + Me_3SiCl + THF;$$
$$M = Cr, Mo, W;\ X = \ t\text{-}Bu_2E(E = P, As), \quad t\text{-}BuS \ .$$
$$(CO)_5M\cdot SnCl_2\cdot THF \xrightarrow{ROH} (CO)_5M\cdot Sn(OR)_2 \ ;$$
$$M = Cr, Mo, W;\ R = H, Et \ .$$
$$(CO)_5M\cdot SnCl_2\cdot THF + Me_3SnOH \rightarrow (CO)_5M\cdot Sn(OH)_2 + Me_3SnCl \ ;$$
$$(CO)_5M\cdot SnCl_2\cdot THF + NaM'(CO)_5 \rightarrow (CO)_5M\cdot Sn[M'(CO)_5]_2 + NaCl + THF \ ;$$
$$M, M' = Cr, Mo, W \ .$$

The stannylene complex evidently can be stabilised also by the coordination interaction of the stannylene with the free electron pair of a halogen atom which functions as the base B̈. Tin(II) dihalides and also certain other stannylenes with electronegative substituents X (electron pair donors) are known[32,34,129] to be capable of forming intermolecular coordinate bonds Sn–X–Sn (Figs. 3 and 4) and to be able to react with electron-donating solvents (Solv.) to form discrete complexes $SnX_2.Solv.$[32,34] The electron pair donor X can be abstracted also from other metal halides, which entails the formation of discrete stable complex anions X_3Sn^- (Fig. 9*a*). The ions X_3Sn^- have a trigonal-pyramidal structure in which all three atoms X and the free electron pair are involved in the sp^3 hybridisation of the tin(II) orbitals[322,323,353].

The high nucleophilicity of the stannylene stabilised by coordination to an anion X^- and the extremely high stereochemical activity of its free electron pair make it possible to obtain stable complexes of the type $M^{n+}(SnX_3)_n$ (Fig. 9*b*) from SnX_2 and alkaline earth metal salts $M^{n+}X_n$ (n = 1 or 2; X = halogen[354–361], acetate[94,353,362], or other anions[32,34,363,364]) and also quaternary oniom salts[133,361,363,365–368]. A characteristic feature of these complexes is the largely ionic character of the Sn–M bond and the high density of the *s* electrons at the tin nuclei and hence also high Mössbauer *IS* values (2.83–4.03 mm s^{-1}).[94,133,355,357–359,365,367–370]

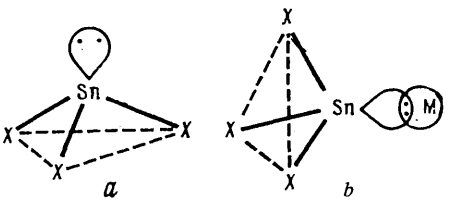


Figure 9. The structures of the anion X_3Sn^- (*a*) and the complex $M^+SnX_3^-$ (*b*).

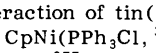
Taking into account the stereochemical activity of the free electron pair in X_3Sn^-, an attempt was made to obtain its complex with BF_3,[371] but it was shown later that in this case a different process takes place[372]:

$$SnCl_3^- + BF_3 \rightarrow (BF_3Cl)^- + SnCl_2 \ .$$

As electron pair donors, the anions SnX_3^- form stable complexes with various transition metal compounds. One of the commonest and simplest methods of synthesis of complexes of the type $X_3Sn.M$ is the reaction of dihalogenostannylenes with transition metal halides, particularly those which contain electron-donating ligands L:

$$SnX_2 + MX\cdot L \rightarrow X_3Sn\cdot M\cdot L \ .$$

Such reactions, which involve the insertion of SnX_2 in a covalent bond M–X, were described above (Section III). When the M–X bond in metal halides is ionic, the interaction of the latter with SnX_2 is ionic, as happens for alkali and alkaline earth metal salts, and also in the reaction of $SnCl_2$ with $(Ph_3P)_3MCl$ (M = Cu, Ag, or Au) in organic solvents[255] or in water[373]. The interaction of tin(II) dihalides with MF_2 (M = Fe, Co, or Ni),[374] $CpNi(PPh_3Cl$,[375,376] $[RuI(CO)_3.(PPh_3)_2]I$,[268] $CpFe(dppe)X$,[377] $(R_3P)_2Pt(CL)H$,[263,378,379,380] and other halogeno-derivatives of transition metals[250,381,382] takes place similarly:



As in the case of stannylenes, one of the methods of synthesis of complexes of type $X_3Sn.M$ involves the displacement of other ligands by X_3Sn^- anions:

$$ML_n + SnX_3^- \rightarrow [ML_{n-1} \cdot SnX_3]^- + L\ ;$$
$$M = Cr, Mo, W, Fe, Co, Ni, Mn, V\ .$$

CO molecules,[257,383–389] π-arene ligands (mesitylene, cycloheptatriene, and benzene),[385,386] acetonitrile[386] and PF_3 [390, 391] molecules, and also halide anions[255,392–399] are displaced in this way. Solutions of mixtures of SnX_2 with R_4EX (E = N, P, or As) or with HX in water or organic solvents[255, 393–399], for example, in ether where the corresponding etherates are formed from SnX_2 and HX,[158,159] can serve in this instance as sources of the ligands X_3Sn^-. The etherates of $HSnX_3$, which are convenient sources of the X_3Sn^- anions, can be obtained successfully by reducing SnX_4 with lithium tetrahydrolaluminate[400]. Other methods of synthesis of complexes of the type $X_3Sn.M$ from quadrivalent tin compounds are also known[268,401–404].

The few available literature data indicate the similarity of the structures of a series of stannylene and carbene complexes[42]. Thus according to structural studies[38], the valence angle of stannylene in the complex $[(Me_3Si)_2CH]_2Sn.Cr(CO)_5$, which is 98°, differs little from the valence angles of free stannylenes, i.e. the tin(II) atom retains the sp^2 configuration. Mössbauer spectroscopic data confirm this conclusion; the isomer shifts *IS* of the free and complexed diorganostannylenes are similar and amount to 2.16 and 2.21 mm s^{-1} respectively[130]. The coplanarity of the stannylene fragment C–Sn–C with the transition metal atom in such complexes ensures the possibility of an additional π-interaction between the occupied 3*d* orbitals of the transition metal and the unoccupied *p* and *d* orbitals of the tin atom, as a result of which the Sn–M bond length is always smaller than the sum of the covalent radii of the atoms of these elements, as in the carbene complexes[42].

Unfortunately there are so far no structural data on complexes of inorganic and organic compounds of tin(II) of the type $SnX_2.ML_n$ (X = halogen or chelate; M = transition metal). Nevertheless it has been suggested on the basis of spectroscopic studies that they have analogous structures and that the anomalous *IS* values in the Mössbauer spectra of these complexes can be accounted for by the synergistic Sn → M σ-interaction and the M → Sn $(d-p)\pi$- or $(d-d)\pi$-interactions along the Sn–M axis (Fig.10).[328,330,405]

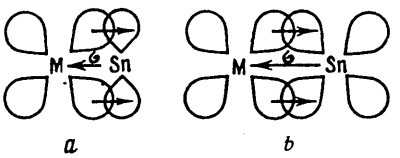


Figure 10. The $(d-p)\pi$-interaction (*a*) and the $(d-d)\pi$-interaction (*b*) of the *p* and *d* orbitals of the tin atom and a transition metal M.

This is confirmed by the absence of appreciable differences between the *IS* values for stannylenes (even dihalogenostannylenes) and their complexes with BX_3 or AlX_3,[98,204,323] which do not have occupied *d* orbitals. However, one cannot rule out the possibility that the appreciable decrease of *IS* in certain complexes of dihalogenostannylenes with transition metals can be accounted for by their ylide structure.

Analogous effects are probably observed in stannylene complexes stabilised by a base B. In the complex $Py(t\text{-}Bu)_2Sn.Cr(CO)_5$, the tin atom projects by only 0.44 Å from the plane passing through the carbon atoms and the chromium

The results of vibrational and Mössbauer spectroscopic and structual studies of certain complexes of the type $Cl_3Sn.M$.

Complex*	*IS*, mm s^{-1}	References	$\alpha(Cl\text{-}Sn\text{-}Cl)^0_{av,s}$	$l(Sn\text{-}Cl)_{av}$, A	l-(Sn–M), Å	References	$\nu(Sn\text{-}Cl)$, cm^{-1}	References
$(SnCl_2)_x$ (crystalline)	4.07	[133]	79	2.74	—	[34, 69]	195	[77]
$H^+[SnCl_3]^-$ (etherate)	3.46—3.54	[140, 159]	—	—	—	—	297, 256	[419]
$Cs^+[SnCl_3]^-$	3.40	[355, 358]	89.8	2.52	4.569	[419]	304, 258	[255]
$[(en)_3Co][SnCl_3]Cl_2$	—	—	92.7	2.488	5.0	[399]	—	—
$SnCl_2$ (monomer in Ar matrix)	3.17	[53]	95±2	2.42	—	[50, 53]	354, 334	[51]
$[(dppe)_2CoCl(SnCl_3)]$	3.10	[382]	94.5	2.444	7.6	[382, 411]	—	—
$[(Me_2PhP)_2AuSnCl_3]$	2.92	[408]	94.9	2.450	2.881	[412]	—	—
$[(chtr)Mo(CO)_2SnCl_3]$	—	—	95.0	2.411	2.72	[413]	—	—
$[(Me_2PhP)_2(nbd)IrSnCl_3]$	2.08—2.16**	[408]	95.5	2.406	2.587	[414]	—	—
$[(cod)_2IrSnCl_3]$	2.06	[408]	96	2.395	2.64	[415]	317, 300, 290	[420]
$[CpFe(CO)_2SnCl_3]$	1.77	[267]	98.3	2.360	2.466	[416]	346, 322	[247]
$[(CO)_5MnSnCl_3]$	1.73	[266]	100.4	2.344	2.59	[417]	345	[421]
$SnCl_4$	0.85	[409]	109.5	2.31	—	[418]	407, 368	[422]

*Notation: en = ethylenediamine, dppe = diphenylphosphinoethane, chtr = cycloheptatrienyl, cod = cyclo-octadienyl, and nbd = norbornadiene.

**The values of *IS* are quoted for isostructural complexes with the phosphine ligand Ph_3P or $(MeO)_2PhP$.

atom linked to tin. The stabilisation of the complex by the base is accompanied by some alteration of the configuration of the tin(II) atom ($sp^2 \rightarrow sp^3$) and a corresponding increase of the C–Sn–C valence angle[406].

In the complexes $X_3Sn.M$, where the role of the base B is assumed by the anion X^-, analogous structural changes should be observed in the dihalogenostannylene fragment. The available data on the Mössbauer spectra, structures, and vibrational spectra of a series of complexes of the type $Cl_3Sn.M$ are compiled in the Table. The large differences between the Sn–M bond lengths in complexes of this type and also the available conductimetric data for solutions of some of them in CH_2Cl_2 or nitromethane[375,376,407] indicate different types of the Sn–M bond, which changes from ionic in complexes of the type $Cs^+[SnCl_3]^-$ to a σ-bond in many complexes with transition metals. In ionic complexes with discrete $SnCl_3^-$ anions, in which the tin(II) atom has a pyramidal sp^3 configuration (Fig. 9*a*), the high value of *IS* is determined by the high density of the *s* electrons at the tin atom, which are not involved in the formation of the Sn–M bond.

A satisfactory correlation between the *IS* values in the Mössbauer spectra, the stretching vibration frequency ν of the Sn–Cl bond in the infrared and Raman spectra, and the structural parameters is observed for the stannylene complexes $Cl_3Sn.M$, in which there is an Sn–M σ-bond. In conformity with the increase of *IS*, the Cl–Sn–Cl valence angle decreases and the Sn–Cl bond length increases in these complexes within the range of limiting values from 109.5° and 2.31 Å for the tetrahedral sp^3 configuration of $SnCl_4$ [418] to 95° ± 2° and 2.42 Å for the sp^2 configuration of free $SnCl_2$ in the vapour phase or in the argon matrix[50,53]. Similarly the shift of the absorption bands of the Sn–Cl bond from the region of lower frequencies characteristic of free $[SnCl_3]^-$ ions in solution[419] to higher frequencies indicates the approach of the SnX_3 configuration in the complexes to the tetrahedral configuration, which is possible with participation of the $5s^2$ orbitals of tin(II) in the formation of a σ-bond with the metal.

The majority of investigators believe that the tin atom in these complexes is in a bivalent state of oxidation; the observed low *IS* values can be explained (as in the complexes $X_2Sn.M$ unstabilised by a base) by the occurrence, apart from the relatively weak Sn → M σ-interaction, of a strong M → Sn $(d–d)\pi$-interaction (Fig. 10*b*). The overlapping of the *d* orbitals of the tin atom and the *d* orbitals of the transition metal leads to additional π-bonding and hence to a decrease of the Sn–M bond length (see Table).

Generalising the results of numerous investigations, one can probably conclude that the *s* character of the sp^x-hybridised orbitals of the tin atom in stannylenes and their complexes, both stabilised and unstabilised by a base, decreases in the sequence

$$sp^2\text{-Sn(II)} > sp^3\text{-Sn(II)} > sp^3d\text{-Sn(II)} > sp^3\text{-Sn(IV)} .$$

The Mössbauer isomer shift *IS* decreases and other spectroscopic and structural characteristics vary in the same sequence.

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During the preparation of the manuscript for the press, numerous studies on the topic of this review were published. In the first place mention should be made of publications describing new sources of diorganostannylenes. This dimethylstannylene was obtained from $(Me_3Sn)_2S$ at 150° to 160 °C in the presence of copper[423].

Certain new monomeric organic compounds of tin(II) and organotin(II) compounds have been obtained and investigated. Free phenylstannylenes, stabilised by *ortho*- or 2,6-substitution (by CF_3, OMe, and t-Bu groups), have been obtained from $SnCl_2$ and the corresponding phenyl-lithium derivative[424]. A cyclic organostannylene has been obtained by the reaction of 1,1-dichloro-3,3,5,5-tetramethyl-1-stanna-3,5-disila-4-oxacyclohexane with magnesium or lithium in THF.[425,426] A series of organic compounds of tin(II), such as $Sn(OAr)_2$ (Ar = 2,6-t-Bu_2-4-MeC_6H_2 or 2,4,6-t-$Bu_2C_6H_2$), [427] $Sn[NCMe_2(CH_2)_3CMe_2]_2$,[428] $(CO)_5WP[P(O)(OEt)_2]_2SnCl$,[429] and $Sn[Al(OPr\text{-iso})_4]_2$ [430] have also been synthesised. Stannylenes forming part of the composition of various polycyclic systems have been obtained from cyclic diazastannylene[431–433].

The study of the synthetic possibilities of stannylenes has been continued. The insertion of $SnCl_2$ in the C–Br bond of allyl bromide under various conditions[434] and also the insertion of a cyclic organostannylene in the C–Cl bonds of alkyl and aryl chlorides and allyl chloride[425] have been described. The insertion of dihalogenostannylenes in the C–I bond of perfluoroalkyl iodides takes place extremely readily (in DMF at 20 °C).[435]

New examples of the insertion of stannylenes in the Hg–X and Hg–C bonds[436], of $SnCl_2$ in the Tl–Cl bonds of compounds of the type R_2TlCl (R = C_6F_5, C_6F_4H, or $C_6F_3H_2$),[437] of $(MeCp)_2Sn$: in the W–H bond of the complex $HW(CO)_3Cp$–Me,[438] of Me_2Sn: in the S–S bond of the complex [μ-dithio)-bis(tricarbonyl iron),[439] of $SnCl_2$ in the N–Cl bonds of the compounds p-$RC_6H_4SO_2NCl_2$ (R = Cl, H, or Me),[440] and of $[(Me_3Si)_2N]_2Sn$: in the N–Br bond of the compound $(Me_3Si)_2$.NBr [441] have been discovered.

As before, the reaction in which the dihalogenostannylenes are inserted in M–X bonds involving transition metals has continued to attract most attention. The interaction of SnX_2 with cobalt and iron complexes containing two M–X bonds has been studied[442]. It was established that the ligand SnX_2, formed when SnX_3 is inserted in the Co–X or Fe–X bond, deactivates the second M–X bond. The employment of modern research techniques makes it possible to solve in such cases the problem of the nature of the product of the reaction of the M–X bond with SnX_2. In some cases insertion products containing a quadrivalent tin atom are formed[443], while in the others the products are complexes with electron-donating ligands $:SnX_3^-$, in which the tin atom is bivalent[444–446]. The reaction in which $[Re(CO)_5]_2Sn$: [447] and a cyclic organostannylene[426] are inserted in the M–M bonds of bis-(metal pentacarbonyl) derivatives of transition metals proved to be extremely effective in the synthesis of mixed polynuclear metal carbonyls.

Numerous studies, in which stannylenes behaved as electron-donating ligands in complexes, have been published. Thus the complexes $Sn(NR_2)_2.nBF_3$ (n = 1, 2, or 3; R = Me or Et) have been described[448]. Stable complexes of SnX_2 with BF_3 have been obtained by stabilising them with electron-donating molecules of the type Me_3N, DMSO, tetramethylethylenediamine, etc. The high Mössbauer *IS* values confirm the bivalent state of the tin atoms in the complexes $F_3B \leftarrow :SnX_2 \leftarrow :Solv$ obtained[449].

A number of investigators have continued to study transition metal complexes of stannylenes both unstabilised[450] and stabilised[451,452] by a base B.

New examples of the substitution of chlorine atoms in dichlorostannylene complexes of transition metals $M(CO)_5$.$SnCl_2$.B, stabilised by a base B, have been reported[453,454].

Finally, it has been reported that organic compounds of tin(II) with benzil give rise to products of the formal 1,4-cycloaddition involving both carbonyl groups of benzil[455]. It has been shown that compounds of this type, 2,2-dialkyl-1,3,2-dioxastannols, are capable of forming dialkylstannylenes on thermolysis[456]. Analogous formal 1,4-cycloaddition reactions involving the carbonyl groups of *o*-benzoquinone are known for cyclohexadiene carbenes[457].

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The Role of Free-radical Oxidation Reactions in the Molecular Mechanisms of the Ageing of Living Organisms

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The review describes the present state of knowledge about the free radical oxidation reaction of biomacromolecules as one of the ageing factors and considers the possible causes of the changes in the rate of ageing and of the prolongation of life in experiments involving exposure to chemical geroprotectants.
The bibliography includes 157 references.

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I. INTRODUCTION

Regardless of the complexity and wide variety of theoretical ideas about the mechanisms of ageing, the majority of gerontologists are unanimous in their view that it can be a consequence of the accumulation of lesions and defects at all levels of the living organisms.

One can point to at least two fundamentally different sources of the breakdown of the functions and of the structural damage to macromolecules. Firstly, errors may arise in the course of the normal functioning of the cell, for example, in the copying of the DNA matrix or in the synthesis of protein as a consequence of the imperfection of the transmission of information from one macromolecule to another. The reliability of the replication of DNA and of the components of the protein synthesising mechanism depends on their molecular structure and is genetically determined.

In this review attention is concentrated mainly on the second source of the impairment of functions as a result of ageing, associated with the random changes in various components of the cell caused by processes involving the oxidative degradation of the macromolecule. The "free radical" hypothesis, which was initially based on the similarity of the radiation-induced and natural ageing processes, was at one time received with reserve by some gerontologists, but it nevertheless proved fruitful because it led to the possibility of influencing the rate of ageing by chemical agents. Radioprotectants and antioxidants are at the head of the list (fairly extensive nowadays) of chemical geroprotectants.

Chemical geroprotectants are widely used as instruments for the study of the mechanisms of the ageing of various objects of experimental gerontology: cell cultures, unicellular organisms, nematodes, insects, mammals, etc. Recognition of the usefulness of antioxidants was reflected, in

particular, in the fact that, during the last decade, the study of the so-called "membrane component" of the mechanism of ageing has become widely popular.

On the basis of an enormous amount of empirical data, the view has been established in the gerontological literature that there exist many independent ways in which age-induced changes accumulate even at the molecular level. This view is difficult to reconcile with the attempts to create a simple and universal theory of ageing and to suggest some way of altering the rate of ageing and the species dependent limits of the lifespan established in the course of evolution.

In the present review we attempted, using our own and literature data concerning the nature of the stochastic damage to biostructures, to justify the view that free-radical oxidation processes constitute a special and all-permeating background against which the metabolic activity of the cell takes place.

II. FREE-RADICAL SPECIES (O_2^-, OH·, $RO_2^·$) AS ENDOGENIC DAMAGING AGENTS

The free radical states of organic coenzymes, mainly semioxidised flavins and the semiquinone forms of ubiquinones localised in mitochondria, cytochrome P-450 functioning in the electron-transport chain of microsomes, as well as haemoproteins, copper-containing proteins, and manganese, molybdenum, etc. complexes, can be relatively readily detected in biological objects by radiospectroscopic methods. There is a direct quantitative relation between the metabolic activity of the tissue and the intensity of the EPR signals[1-3]. Attention has been devoted in a number of studies[4-6] to the changes in the concentrations of these metabolic free radicals during ageing. The involvement in the ageing mechanism of free radicals whose source is non-enzymatic reduction of oxygen, resulting in the formation of paramagnetic species such as the hydroxy-radical, the superoxide radical-ion, and the peroxy-radical (OH·, O_2^-, $RO_2^·$), appears to be more appreciable. The O_2 reduction reactions are presented below:

$$O_2 + e^- \rightarrow O_2^{\cdot-}$$
$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$$
$$O_2 + 3e^- + 3H^+ \rightarrow H_2O + OH^·$$
$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$

The complete reduction of oxygen to water requires the participation of four electrons, while in the remaining cases partial reduction products are formed: hydrogen peroxide and the radical species O_2^- and OH·, whose high reactivity is the main cause of the toxic properties of pure oxygen.

Attention has been drawn to the fact[7] that the prebiotic atmosphere of the Earth did not contain free oxygen, which appeared in it as the product of the vital activity of photosynthesising blue-green algae. The origin, propagation, and certain initial stages of the development of life took place in an atmosphere lacking oxygen, whose appearance could not fail to influence evolution.

Oxygen accumulating in the atmosphere and the world ocean led to new possibilities for its utilisation by living organisms in biosynthetic processes and energetic reactions but at the same time it constituted a definite threat to the very existence of life. Obligatory anaerobes, which live in the absence of oxygen and have no means of protection against the free radical toxic products of its reduction, are destroyed in air[8]. For all respiring organisms, oxygen, which maintains their life, is at the same time toxic; they exist in its presence solely as a result of definite protecting systems which arose during evolution and function so effectively that the toxic properties of O_2 have attracted the serious attention of scientists only comparatively recently in view of the analogy between oxygen poisoning and radiation damage[9].

It is possible to formulate briefly the general postulates reflecting the fundamental features of the "free radical danger" in the following manner:

(1) Non-enzymatic O_2 reduction reactions constitute the background against which all processes involved in vital activity take place;

(2) oxygen-containing free radicals are the cause of the oxidative degradation of biological macromolecules;

(3) by virtue of their high reactivity (the rate constants for the interactions of the OH· radical are close to the diffusional values), the free radicals do not require a specific substrate for their reactions, the site which they attack is random, and they can damage any unit in the molecular structure of the cell;

(4) transition metals (Fe, Cu) play the role of catalysts of peroxide oxidation.

It can now be claimed that the "free radical" hypothesis of ageing proposed in the 1950's[10] refers to a small number of ideas in gerontology which have withstood experimental tests. Indeed, following self-evident logic, one may expect the acceleration of ageing with increase of the concentration of free radicals, which can be readily achieved by chronic irradiation or by an increase of O_2 pressure. Exposure to ionising radiation is one of the most effective methods for the experimental acceleration of ageing. On irradiation by sublethal doses, explicit signs of radiation damage do not arise in animals (with the exception of the early greying of hair) but their lifespan is shortened in proportion to the size of the dose. An example of the acceleration of ageing in Drosophila males irradiated at the age of one day by γ-ray doses of 80 and 40 krad has been quoted in a monograph[11]. Doubling of the dose shortens the average lifespan of the flies by a factor of two. Analogous data are available for laboratory mice and rats[12]. There is no complete identity between natural ageing and the reduction of the lifespan induced by radiation[13], but analysis of the causes of the death of the irradiated animals showed that they die due to the same illnesses as the non-irradiated animals, although the relative frequencies of the different illnesses may not be the same. Thus, presumably at least some of the damage due to radiation is similar to age-induced changes.

An increase of the O_2 concentration in air also leads to an appreciable decrease of the lifespan of Drosophila, which is accompanied by an intense accumulation of the "age pigment" (lipofuscin) in the tissues of the flies, which indicates the activation of the free-radical oxidation[14]. In this case the average lifespan of the flies fell from 78.1 to 34.6 days and their viability decreased much faster than in the control. The study of their tissues under light and electron microscopes revealed the presence of large accumulations of ceroid lipofuscin in the internal organs, consisting of dense lamellar bodies, and the breakdown of cytoplasmatic membranes in the nerve tissues.

The ageing process in cultured cells also proved sensitive to changes in the oxygen concentration. When human diploid fibroblasts were cultured under a high O_2 pressure up to 50 atm, a retardation of the rate of cell division and of capacity for the formation of colonies, particularly in later stages, was observed. On the other hand, if the same pressure was established with an excess of nitrogen, there was no effect on the viability of the cells, i.e. the observed decrease of the capacity for proliferation is a consequence of the toxicity of the O_2 and not the increased pressure[15].

Another method of accelerating free-radical oxidation, by enriching the diet in unsaturated readily oxidisable fats, was used in other studies. An increase in the amount and degree

of unsaturation of fats reduced the average lifespan of mice and increased the frequency of malignant tumours[16]. When two strains of Drosophila were maintained on a medium in which glucose was replaced by palmitic acid, vegetable oil, margarine, etc., keeping the calorific value of the feed at a constant level, a decrease of the average lifespan proportional to the amount of added fat was observed. If the flies were transferred from the fat-enriched diet to the standard diet, their mortality diminished but not all the changes induced by the introduction of excess fat into the diet were reversible[17].

On the other hand, a decrease of the intensity of the free-radical reactions in the organism retards ageing and increases the lifespan. The results of these studies will be presented in the concluding section of this review in connection with the discussion of the mechanism of the action of geroprotectants.

In a more careful examination of the reaction of oxygen-containing free radicals, account must be taken of specific features of their interaction with the cell components. The interaction of the superoxide radical-ion $O_2^{\cdot-}$ with hydrogen peroxide leads to the formation of the radicals OH· and singlet oxygen whose molecule carries excess energy[18]:

$$O_2^{\cdot-} + H_2O_2 + H^+ \rightarrow OH^{\cdot} + H_2O + O_2^*$$

$$O_2^{\cdot-} + H_2O_2 \rightarrow O_2 + OH^- + OH^{\cdot}$$

The spontaneous dismutation (disproportionation) of $O_2^{\cdot-}$ leads to the reformation of hydrogen peroxide[19]:

$$O_2^{\cdot-} + O_2^{\cdot-} + 2H^+ \rightarrow O_2 + H_2O_2$$

the rate constant for this reaction at pH 7.4 amounting to 10^5 s^{-1}.

Numerous spontaneous and enzymatic oxidation reactions, generating considerable amounts of $O_2^{\cdot-}$, are known: autoxidation of reduced flavins, hydroquinones, catecholamines, ferredoxins, and haemoproteins, enzymatic processes with participation of xanthine oxidase and many flavin hydrogenases, etc.[20,21] The superoxide radical-ion reacts as both a reductant and an oxidant. It participates in reactions involving the reduction of cytochrome c, Nitro Blue Tetrazolium, tetranitromethane, etc. and also oxidises sulphydryl compounds, sulphites, ascorbic acid, etc. The reduced NADH when linked to lactate dehydrogenase is readily oxidised by the $O_2^{\cdot-}$ radical-ion, while free NADH is oxidised more slowly[22].

The enzymatic dismutation of $O_2^{\cdot-}$ to hydrogen peroxide and oxygen is effected by the enzyme superoxide dismutase (SOD); the cytoplasm of the cells of eukaryotes contains SOD incorporating copper and zinc and its participation in the disproportionation reaction of the $O_2^{\cdot-}$ radical-ions makes the latter take place up to the theoretical diffusion limit, the rate of spontaneous dismutation being exceeded by a factor of approximately 20000. SOD protects the cell from the toxic action of the $O_2^{\cdot-}$ radical-ion and the OH· radical, which is even more reactive and arises on interaction of hydrogen peroxide with $O_2^{\cdot-}$ or bivalent iron salts[23,24].

The oxidative decomposition of the lysosomal membrane has been observed[25] and it has been established that the cause of the decomposition is free-radical reactions initiated by the superoxide radical-ion, formed on oxidation with reduced flavoprotein of liver microsomes. The authors showed that the $O_2^{\cdot-}$ radical-ion does not itself react with the membrane and that the direct participant in the chain oxidation reactions of the membrane lipids is OH· formed in the presence of ADP and Fe^{3+}. The presence of SOD prevents the breakdown of lysosomes.

Ascorbic acid can be used as a reductant for the ADP–Fe^{3+} complex which is more effective than superoxide, which apparently accounts for its role as the promoter of peroxide oxidation in those cases where vitamin C is used in doses known to be many times greater than the physiological dose[26].

Using the oxidation of xanthine by xanthine oxidase as the source of superoxide radical-ions, measurements were made of the rate of oxidation of vitamin E; the rate constant for the interaction of $O_2^{\cdot-}$ with α-tocopherol proved to be fairly large (1.7×10^{-4} mol^{-1} s^{-1}), which enabled the authors to postulate that the α-tocopherol built into the membrane can trap the $O_2^{\cdot-}$ radical-ions and prevent the initiation of the lipid oxidation[27]. The coefficient of the permeability of the two-layer lipid membrane to oxygen radical-anions is close to the coefficients of permeability to other ions[28]. On irradiation, stimulation of peroxide oxidation, and in inflammatory processes, the depolymerisation of the synovial liquid and of purified preparations of hyaluronic acid, occurring with participation of the $O_2^{\cdot-}$ and OH· radical species, was observed. SOD and catalase have a protecting effect[29,30].

Many aspects of the role of superoxide dismutase in the ageing process still remain obscure. Some information can be derived from data concerning the age-induced changes in the activity and properties of SOD. Much work in this field has been done by Reiss and Gershon[31], who were able to observe differences between the properties of the purified enzyme isolated from the livers of young and old rats. The "old" enzyme was 1.5 times less active than the "young" enzyme, although their kinetic properties were identical. The inhomogeneity of the "old" enzyme, which included a thermolabile fraction absent from the specimen of the "young" enzyme, was discovered in the study of thermal inactivation. Thus SOD supplemented the list of "inactive" enzymes (it includes enzymes such as aldolase, glucose-6-phosphate dehydrogenase, isocitrate lyase, etc.[32]).

Few data are available concerning the changes during ageing of the activity of SOD in the tissues of laboratory animals. Sometimes the age differences are quite distinct, but instances are known where they are absent. The activity of cytoplasmatic SOD in the hearts and livers of 34-month old mice was reduced by 50% compared with 3-month old mice. The same pattern was observed in 40-day old and 4-day old nematodes[33]; in the mouse brain tissues the activity of this enzyme decreases by 32–36% (relative to the protein or DNA content) in the range 50–900 days[34]. No changes were found[35] in the activity of SOD in 3-month and 2-year old rats, but an appreciable increase of the activity of catalase and glutathione peroxidase was noted.

The simultaneous decrease of the efficiency of the generation of $O_2^{\cdot-}$ and of the activity of SOD in the livers of old rats has been demonstrated[36], which enabled the authors to suggest the retention in the cells of a balance between free radical generation processes and the protecting reactions tending to inhibit the stochastic oxidation.

Opposed views have been expressed concerning the question whether or not superoxide dismutase can be regarded as an adaptive enzyme. An increase of the activity of this enzyme has been observed under the conditions of hyperoxia in human lung tissues[37] and also under the influence of the dye methylviologen, which is able to increase the intracellular concentration of the $O_2^{\cdot-}$ radical-ion[38]. After prolonged irradiation with moderate doses, no decrease in

the SOD activity in the tissues of Drosophila and rats was observed[39]. When more severe conditions reproducing the peroxidation syndrome were generated experimentally by maintaining rabbits on a diet lacking exogenic antioxidants, an increase in the activity of SOD was observed[40,41]. The latter study established a monotonic decrease of its activity with age; assuming that the SOD activity in the livers of sexually immature rats is 100%, the following data were obtained: 50% activity in 8-month old rats, 18% activity in 23-month old rats, and 15% activity in 30-month old rats.

In the course of the preimago development of Drosophila, the SOD activity increases by a factor of 3.5, but in the imago it hardly changes with age (in relation to the entire body weight)[42]. The activity of the mitochondrial enzyme reaches a maximum in 8-day old Drosophilas and then decreases by 21% in the course of the next 50 days. One cannot rule out the possibility of detecting age-induced changes in the SOD activity in various organs and tissues of the adult insect. In a mutant strain of Drosophila with an appreciably reduced lifespan the activity of cytoplasmic SOD was always lower than in the wild flies[43].

Interesting data were published in a communication[44] dealing with the study of the life cycle of a mutant of *Neurospora crassa* with a short lifespan. In the ageing stage an EPR signal due to the superoxide radical-anion with $g = 2.02$ was detected. In the presence of nordihydroguaiaretic acid as the antioxidant, the intensity of this signal diminished, but at the same time there was an increase in the intensity of the signal of high-spin Fe with $g = 5.45$. According to the author, the antioxidant accelerates the conversion of O_2^- into hydrogen peroxide, inducing the synthesis of catalase with which the $g = 5.45$ signal is associated.

In cultured strains of diploid human cells, which have only a limited lifespan and are usually regarded as a model for cell ageing[45], the observed changes in the SOD activity do not as yet permit an unambiguous interpretation. In cells whose source was embryonic lung tissue the SOD activity did not change in the course of the last 30 passages, the life of the culture[46]. According to other data[47], the greatest increase in the activity of superoxide dismutase occurs in the early stages of the growth of the culture, from the tenth to the twentieth passage. In the above study the specific activity of SOD was measured in the cells of diploid cultures obtained from adult donors; a significant increase of activity with increase of the number of times the population doubled was noted for strains derived from cells of embryos or the newborn but the maximum (and constant) activity of SOD proved to be characteristic of cells in cultures derived from the tissues of adult humans. Simultaneously with the increase of the SOD activity in the cells of the skin of the newborn, the rate of protein metabolism diminished and the fraction of thermolabile enzymes and the rate of reparative synthesis of DNA increased against the background of the accumulation of oxidation products. The authors are inclined to assume that the SOD activity in the old cells increases in response to the activation of the free radical oxidation processes.

Thus at the present time there are numerous facts showing that the enzymes superoxide dismutase, catalase, and glutathione peroxidase, which eliminate O_2^-, H_2O_2, and organic peroxides, play the role of the most important cell protecting systems together with natural antioxidants. The factors having a negative or positive influence on the lifespan of mammals have been arranged systematically[48]. Among the negative factors (there are 10 in all), the second place is taken by the accumulation of the age pigment lipofuscin, which is formed in the free radical oxidation of the lipid and protein components of biomembranes according to the majority of gerontologists. In the list of the positive factors (there are 18) the first place is occupied by DNA reparation processes and is followed in order of importance by the antiradical (enzymatic and antioxidant) protecting systems.

The possible role of SOD in determining the longevity of mammals has been investigated[49]. Its specific activity was measured in the cytoplasm of the liver, brain, and heart of two species of rodents, eleven species of primates, and man; the range of the changes in the maximum lifespan was from 3.5 to 95 years. The SOD activity in the tissues of animals of one species was the same but in different species its level differed by a factor greater than two and was a maximum in man. The age-induced changes in activity are not clearly expressed in all the species. The ratio of the SOD activity to the specific metabolic rate in a given tissue or the whole organism (the metabolic rate was determined from the absorption of O_2) increases with the maximum lifespan in all the species. This correlation suggests that in the long-lived species there is a more effective protection against the side products of the O_2 metabolism. Here it is appropriate to mention the results of a search for a relation between the lifespan and the anatomic-physiological parameters of the organism[50]. It has been shown by the method of multiple regression for 85 mammalian species that the lifespan is determined by only two independent parameters: the "cephalisation index", i.e. the ratio of the weight of the brain to the body weight, and the intensity of the metabolism (calculated from the absorption of O_2 at 37 °C). The equation obtained shows that the lifespan is longer the higher the cephalisation index and the lower the metabolic rate (the longer the period of development associated with it). According to Cutler[48], the increase of lifespan in the evolution of mammals occurred as a result of the selection and improvement of the protecting systems and "life support processes" (the opposite of ageing), which led, in particular, to the increase of the period of development in the long-lived species.

It is not possible to consider within the framework of this review another aspect of the biological role of H_2O_2 and O_2^-, whose high reactivity is used by the cells for protection against unfavourable factors. It is known, for example, that phagocyte-producing leukoctyes contain 2–4 times more H_2O_2 and generate O_2^- more actively than the non-phagocyte-producing polymorphic-nuclear cells[51]. We shall confine ourselves to listing the literature references on this question[20–22,24,52].

The enzymatic dismutation of O_2^- radical-ions results in the formation of water and oxygen in the triplet state. The spontaneous disproportionation reaction leads to the formation of a hydrogen peroxide molecule, which reacts in its turn with another O_2^- radical-ion, giving rise to singlet oxygen and the OH· radical. The molecule of singlet oxygen reacts with the biosubstrate by virtue of its excess energy and initiates new free radical oxidation centres. The damage to the DNA molecule by singlet O_2 has been investigated[53]; a review has been devoted to the role of singlet oxygen in the pathology of cell membranes[52]. The known producers of singlet oxygen, namely NaOCl and the 3-AT herbicide, the latter inactivating catalase with the consequent accumulation of excess H_2O_2 in the tissues, were added to the Drosophila feed. The average lifespan then decreased by 25–29%. The simultaneous addition of large doses of O_2^- quenching agents, namely β-carotene and 1,4-diazabicyclo[2.2.2]octane, had some protecting effect but it could not fully prevent the negative influence of the sources of O_2^-. The quenching agents did not exhibit the properties of geroprotectors, i.e. they did not retard the ageing of intact flies. On this basis, it has been concluded[54] that the role of singlet oxygen in natural ageing is insignificant and becomes appreciable only in those cases where its high concentrations are created artificially.

III. THE CONTRIBUTION OF PEROXIDE OXIDATION PROCESSES TO STOCHASTIC MECHANISMS OF AGEING

There exists an extensive literature on the relation between ageing processes and the peroxide oxidation of lipids, which also have a definite place in the normal vital activity of the cell[6,55-59]. In contrast to mitochondrial oxidation, which serves mainly as a source of energy, the role of peroxide oxidation is associated primarily with the formation of active metabolic products involved in the reactions of lipids—the main substrates of peroxide oxidation. The rate of peroxide oxidation is regulated by many factors, which can both initiate the process (pro-oxidants) and inhibit it. The structure of the protecting mechanisms, which protect the cell against the excess accumulation of toxic oxidation products, is usually believed to comprise two stages[60]. The first involves antioxidants, which react directly with free radicals and the second involves enzymes and non-enzymatic components, which reduce hydroperoxides and which were partly examined in the previous Section. In another study[61] an additional antioxygen protecting stage was introduced. The relevant function is fulfilled mainly by compounds of the type of carotenoids, which absorb the excess of free oxygen and maintain the O_2 pressure in the cell within the physiological limits.

The concentration of endogenic lipid peroxides in tissues is determined by the ratio of their formation and decomposition. In the cell membrane there is a constant content of lipid peroxides on the concentration of which the permeability of the membrane depends. In rat liver, for example, the normal concentration of lipid peroxides does not exceed 10^{-7} mole. The biosynthesis of hormones such as the prostaglandins proceeds via a stage involving the formation of unsaturated acid peroxides[62]; in the synthesis of cholesterol and steroid hormones, squalene oxide is formed as an intermediate[63].

Studies relating the lipid metabolism to the rate of cell division are of great interest. Analysis of extensive factual data led the authors of a book[64] to the conclusion that the decrease of the proliferative activity of cells is accompanied by a decrease of the amount of their natural antioxidants and an increase of the intensity of free radical reactions. The role of cell division inhibitors is usually attributed to lipid peroxides. These observations serve as a basis for the hypothesis of a free radical mechanism of the regulation of cell division which is very labile and sensitive to a wide variety of external influences which alter the concentration of natural antioxidants, the lipid composition, the rate of initiation of free radical reactions, etc. The presence of antioxidants in the lipid phase of the membrane is nowadays regarded as an obligatory condition for the maintenance of its structure, while peroxide oxidation reactions of lipids lead to its breakdown. One cannot rule out the possibility that vitamin E also plays a structural role[65-67].

An important place in the biochemistry of peroxides has been assigned[68] to their interaction with proteins, assuming that the NH_2 and sulphydryl groups (the latter are oxidised to disulphide groups) are the most vulnerable; not only peroxides but also the product of their further reactions, for example, epoxides, form insoluble complexes by combining with proteins. The above communication lists 15 enzymes whose activities are inhibited by lipid peroxides, including the enzymes involved in glycolysis, the tricarboxylic acid cycle, and the respiratory chain. Ribonuclease A, which contains no SH groups, is nevertheless inactivated by the products of the oxidation of unsaturated aliphatic acids, the inactivated enzyme containing high-molecular-weight polymers, whose fluorescence spectrum is identical with that of lipofuscin accumulating in senile heart muscle[69]. Interaction with lipid peroxides causes the degradation of catalase, γ-globulin, haemoglobin, egg and serum albumins, methionine, histidine, and other aminoacids[70].

Structures most vulnerable to oxidative breakdown are the microsomal and mitochondrial membranes in which are located enzymes such as monoamino-oxidase or microsomal cytochrome oxidase, whose normal function is catalysis of the oxidation by oxygen. The destabilisation of membranes as a result of the local interaction of lipids with metabolic or exogenic free radicals converts them into a substrate readily susceptible to oxidation. When suspensions of rat liver mitochondria were treated with a solution of bivalent iron salts, the activation of free-radical oxidation was observed, which resulted in the loss of approximately 65% of mitochondrial protein and of 40% of lipids. Induction of peroxide oxidation leads to the complete inactivation of isocitrate dehydrogenase, 3-hydroxybutyrate dehydrogenase is 80% inactivated, and malate and succinate dehydrogenases are 36 and 23% inactivated. Oxidative phosphorylation breaks down[71]. A secondary consequence of the partial oxidation of the unsaturated aliphatic acids of the membrane is their replacement by saturated lipids, which alters the permeability and functional properties of the membranes; the affinity of the membranes of microsomes for cholesterol diminishes and a deficiency of the latter arises[72,73].

The breakdown of the biological mechanism of the inhibition of free radical oxidation may be the factor initiating the development of pathological conditions such as radiation sickness, atherosclerosis, and tumours[2,4,74]. Ageing, regarded as the experimental syndrome of lipid peroxidation, is characterised, according to Voskresenskii's definition[75], by a "tetrad" of features—damage of the membranes, inactivation of the enzymes, breakdown of cell division, and the accumulation of ballast polymers. Experimentally recorded deviations at the physiological, cellular, and subcellular levels, whose origin is damage of the membrane during the ageing process, have been listed in a review[72]. The most significant of these are the breakdown of the permeability of the cell membranes, the appearance of microsomes and mitochondria with heterogeneous structures and properties, a decrease of the amount of cholesterol in the liver microsomes of old animals, a decrease of the efficiency in relation to endocrine effectors such as insulin and catecholamines, whose physiological activity depends on the stereospecificity of the interaction between the hormone and the receptor, and the accumulation of the transoxidation products in the cells and in the blood.

The search for a criterion of the ageing of human diploid fibroblasts, cultured routinely outside the organism, has led to the conclusion[76] that the "imprint of age" is most appreciably reflected in the properties of the cell membrane. By fractionating a normal cell population which has lived through 20 passages *in vitro*, the authors obtained several subcultures consisting of cells of identical size and traced their transition to the ageing phase. It was found that ageing parameters frequently employed such as cell size, the volume of the nucleus, the intensity of the incorporation of thymidine, the DNA content, etc. are poorly correlated with the age of the culture. As the cell ages, the adsorption properties of its surface change; concanavalin A, bound to erythrocytes, is weakly adsorbed by cells of young cultures; the adsorption intensity increases linearly with the number of passes and is independent of the cell cycle phase and the metabolic age.

Thus the main source of the structural and functional disorders arising in ageing may consist in the breakdown of the steric and cooperative interactions in the cytoplasm, in the matrix, in the membranes of organelles, and on the surfaces of cells. The activity of membrane enzymes, reception,

and permeability depend on these properties, which determine the specific organisation. If the properties undergo irreversible changes or are lost, then, even with a correct programme of synthesis, the functioning of the cell is difficult owing to the impaired efficiency of the endocrine receptors or modulators ensuring the reliability of the transport of metabolites.

The maintenance of the relative constancy of the internal medium within the organism is one of the obligatory conditions for existence. The constancy of the physiological level of free radical oxidation reactions is achieved mainly by antioxidants, among which the main role is played by vitamin E whose distribution and metabolism have been adequately studied mainly in connection with the E vitamin deficiency[64, 65,68,75,77-82]. The need for vitamin E and other antioxidants changes in the course of life. The content of vitamin E in the blood, livers, and skeletal muscles of sexually immature rabbits and rats progressively increases during growth, in the adult animals a relative stabilisation is observed, while in the old animals there is a decrease. The latter may be associated with the intense breakdown of antioxidants in oxidation reactions and their inadequate assimilation. Compared with 30-year old humans, in 60–70-year-old individuals the concentration of vitamin E in the blood plasma is reduced to 60%.[83] According to Leibovitz et al.,[84] during the ageing of stable strains of mice and New Zealand black mice with a hereditary defect of the immune system, a redistribution of ascorbic acid in the liver and spleen tissues is observed. In immunodeficient mice the level of vitamin C in the spleen tissue decreased during the period preceding the development of the autoimmune sickness. A steady decrease of the antioxidant activity of lipids with age has been recorded[85,86]; it is significant that the rate of decrease of this quantity was greater for short-lived mice. The change in the rate of formation of lipid peroxides in rat microsomes during ageing has been described[87]; in the presence of ascorbate the rate of oxidation increased non-uniformly with age: at the age of 600 days it was lower than at the age of 400 days but exceeded that in the young animals. The author explains this observation by the decrease of the efficiency of the monoxygenase microsomal system in old rats.

The data concerning the age-induced changes in the intensity of peroxide oxidation in the subcellular fractions of tissue homogenates are contradictory; a decrease of the accumulation of malonic dialdehyde under the conditions of the induced oxidation of the microsomal, mitochondrial, and postnuclear fractions of the livers of old rats has been reported recently[88,89]; oxidation was retarded with increase of the protein concentration.

Many facts indicate a functional relation between different units of the antioxidant protecting system in cells. The activity of the glutathione peroxidase of erythrocytes, which reduces lipid peroxides, depends on the vitamin E content of the blood[90]. The concentration of reduced glutathione in mouse erythrocytes decreases both on ageing of the red cells themselves and on ageing of the organism. In old mice (31 months) its amount in the liver, kidneys, and heart muscle is lower by 30, 34, and 24% than in the 17–23-month old animals. Involution of the thymus in mice is accompanied by a depletion of its tissues in coenzyme Q (ubiquinone), which is lost to the extent of 80% by the age of two years, and this leads in its turn to the almost complete inactivation of succinate dehydrogenase in this organ[91,92].

It has been concluded[75] that the biological inhibition of free radical reactions in the organisms, which takes place via a series of interacting oxidation-reduction reactions of tocopherols, glutathione, and ascorbate, is systemic in nature.

The SH-containing proteins, whose concentration in the human blood plasma decreases with age almost by 30%, belong to the class of natural antioxidants[93]. There is now no doubt that the status of vitamin E in the organism is associated with the biochemical function of selenium compounds; when there is a deficiency of selenium in food, the metabolism of tocopherols and the catabolism of the proteins in the liver microsomes are accelerated[94].

When there is a deficiency of vitamin E or after prolonged hyperoxia, distinct changes arise in the morphology of cells, particularly non-dividing cells. Lipofuscin is formed in the cytoplasm of the nerve and muscle cells and accumulates in the form of small yellow or brown granules with a characteristic weak fluorescence. Lipofuscin or the "age pigment" is regarded by many gerontologists as the best indicator of age; the linear relation between age and the content of lipofuscin in the human myocardium established by Strehler[95] is generally known. There is an extensive literature on the origin of the lipofuscin grains and their biochemical properties and biological role[96-98], which makes it unnecessary to describe the problem in detail. Numerous data on the structural and biochemical properties of lipofuscin have shown that free radical oxidation reactions of membrane lipids and proteins may be the source of its formation. It is known that on ageing and under unfavourable conditions (stress and poisoning), the membranes are depleted in natural antioxidants. On oxidation of the membranes of mitochondria, microsomes, and lysosomes under model conditions, phosphatidylethanolamine is "cross-linked" by malonic dialdehyde with formation of a fluorescent product; in animals fed a diet lacking vitamin E, lipofuscin accumulates in various organs faster by a factor of 1.5–6.[97] An increase in the number of lipofuscin grains towards the end of the life cycle of cultured normal cells has never been observed. Human diploid cells are in stage III of growth after 40–42 passages and contain approximately 80% of non-dividing cells; secondary lysosomes of the type of residual bodies accumulate in such cells; by analysing X-ray scattering, it has been found that the residual bodies contain large amounts of iron[99].

The way in which the accumulation of lipofuscin grains affects cell functions remains a controversial question. Large accumulations of lipofuscin can themselves hinder the functioning of the cell, particularly of neurones, in which the content of endogenic lysophosphoglycerides, exhibiting a detergent effect on the membranes, increases with age and also under the conditions of an incomplete diet or an irrational administration of drugs. Electron microscope studies on the tissues of various sections of the brains of patients suffering from neuronal ceroid lypofuscinosis who died at the age of 7.5–22 established a characteristic accumulation of large masses of lipofuscin in the nerve cells at a young age. The characteristics of premature ageing (loss of vision, extensive pigmentation of tissues, muscular atrophy) also accompany this hereditary disease[100]. Measurements have been made[101] of the average percentages of the volume of the large human neurone occupied by the nucleus, the cytoplasm, and lipofuscin at different ages. At the age of 40, these percentages are in the proportions 1:2:2, i.e. cytoplasm has already been half-absorbed by lipofuscin; at the age of 60 and 80 the volume of the nucleus does not change but the volume of the functioning cytoplasm decreases by factors of 1.3 and 2; in humans who have reached the age of 100 the volume of the nucleus diminishes by 60% (compared with 40-year old individuals) and lipofuscin occupies more than 80% of the overall cytoplasmic volume. The accumulation during ageing of lipofuscin and amyloid and the increase of the number of senile end-plates has been demonstrated by electron microscopy in 17 sections of human brain[102]. The authors of this study

believe that the nature of the age-induced changes and their consequences for the organism depend on the type of tissues and attribute the role of the main regulator of the rate of ageing—the "biological clock"— to the cells of the central nervous system. The non-uniform accumulation of lipofuscin in different sections of rat and mouse brains is indicated by the data of Reichel et al.[103] In the hippocampus of old rats and mice the accumulation of the pigment begins much sooner (from the age of 9–11 months) and is much faster than in the Purkinje cells and in the brain cortex. The pigment occupies less than 0.6% of the surface of the section in the layer of granular cells of the cerebellum in rats and mice of all age groups.

The ageing of insects is also accompanied by the accumulation of the ageing pigment. The low content of tocopherols and the absence of glutathione peroxidase are the cause of the relatively high rate of peroxide oxidation in the cells of the honey bee. The evolution of pentane, formed as a result of the cleavage of unsaturated aliphatic acid hydroperoxides and the age dependent increase of the concentration of lipofuscin in the cells of the thoracic segment in worker bees have been recorded[104]. Measurements have been made of the content of fluorescent substances in the tissues of house flies aged 1,4,11, and 15 days and an increase of their concentration with age was observed, the greatest amount being extracted from neurones. Analysis of the absorption and emission spectra of their complexes with europium made it possible to identify the fluorescent pigments as conjugated Schiff bases; their localisation in the lipofuscin grains was discovered by means of fluorescence microscopy[105]. New data, confirming the role of lipofuscin as the cellular marker of physiological age, have been obtained in studies where the rate of ageing was varied experimentally[106,107]. Flies belonging to a highly inbred strain were separated into two groups in one of which flying activity was restricted, which increased by a factor greater than two the average and maximum lifespans. The relative contents of lipofuscin in the giant neurones in the brains of flies of different ages were determined by electron microscopy and spectrofluorimetry. The rate of accumulation of the pigment in short-lived flies with a high flying activity was four times greater and its maximum content (the same for both groups) was attained sooner.

However, one cannot ignore studies whose authors adhere to the directly opposite point of view, regarding the accumulation of lipofuscin as adaptive and assuming that the age pigment is a normal structural component of the cell. There is a view[108] that the inclusions of lipofuscin are identical with the carotenoid-containing cytosomes in the neurones of molluscs, which function as an intracellular depot of oxygen in certain lower animals which exist permanently under the conditions of hypoxia. This view is shared by the authors of a book[109] who regard the accumulation of lipofuscin as an adaptive process partly balancing the hypoxic state of the cell on ageing. It is known that the oxygen tension in the tissues decreases in elderly and old individuals which is apparently associated with the age-dependent decrease of the level of energy metabolism. At the same time the activation of free radical oxidation reactions inhibits tissue respiration by damaging the mitochondria and the biological oxidation enzymes. The decrease of the consumption of oxygen in the late stages of ontogenesis by no means indicates a decrease of the need for O_2 and may represent the result of the breakdown of its utilisation. According to Voskresenskii and Levitskii[68], there exists an antagonistic interaction between the enzymatic oxidation and the peroxide oxidation involving a free radical mechanism. Under the optimum conditions of the functioning of the oxidative enzyme systems of the cell, the possibility of the formation of lipid peroxides diminishes and, conversely, on ageing the direct oxidation of lipids is enhanced as a result of the decrease of the utilisation of O_2 in energetic processes.

The possible protecting role of vitamin E in acute experimental hypoxia is indicated by a study[110] in which an increase of the concentration of tocopherols in the adrenal tissue was observed, which leads to release of the reserves of adrenalin, a decrease of the intensity of the stress response, and a decrease of the consumption of O_2 by the tissues.

Among the pathological states characteristic of elderly individuals, the most common is undoubtedly atherosclerosis, the development of which may be associated with a change in the antioxidant status of the organism. The results of studies employing experimental models of atherosclerosis are of interest. When animals are maintained for a long time on a fat-rich diet lacking antioxidants, a decrease of the parameters of the functional activity of the antioxidant system and the development of the biochemical and morphological signs of atherosclerosis are observed. As the severity of the disease increases there is a rise in the concentration of total lipids, lipid peroxides, and malonic dialdehyde in the blood, and the wall of the aorta is degraded. The employment of antioxidants makes it possible to regulate their supply to the organism and to retard the development of atherosclerosis. Tests on ionol, hexahydro-4-ubiquinol, quercetin, sodium selenite, and vitamins P, E, and C showed that the action of these compounds is associated with the inhibition of peroxide oxidation and protection against the oxidative degradation of the elastic fibres of the arteries[111–113].

IV. CHARACTERISTICS OF THE ACTION OF ANTIOXIDANT GEROPROTECTANTS

Several careful reviews[114–117] and also one of the chapters in Comfort's monograph[118] were devoted to the mechanisms of the action of chemical geroprotectants of different classes, which enables us to avoid a detailed description except for antioxidants which we believe to be the most promising geroprotectants. The compilation published in 1975[119] of the geroprotectants known at the time must be supplemented by several new compounds. Lactic and gluconic acids, which are inhibitors of the OH' radical, as well as sodium and magnesium salts of thiazolidinecarboxylic acid (antioxidants) retard the ageing of Drosophila and laboratory mice[120,121]. Succinic acid, which acts on the energy balance of the cell, proved to be active[122]. Diphenine (5,5-diphenylhydantoin-sodium), phenformin (1-phenylethylbiguanide hydrochloride), and the polypeptide extract from epiphysis are able to reduce the threshhold of the sensitivity of the hypothalamo-hypophyseal complex to regulating influences, to decrease the frequency of spontaneous tumours, and to increase the lifespan of the experimental animals[123,124]. Inhibitors of the biosynthesis of protein—olivomycin, actinomycin D, and morphocycline—constitute a new group of chemical geroprotectants with a specific mechanism of their action[125,126].

In most cases whether or not a substance is a geroprotectant is determined by the set of properties characterising its biological activity and not its chemical structure or some one property. In this respect antioxidants have been studied in greatest detail. The free-radical hypothesis involves the postulate that antioxidants retard the ageing process because they prevent the accumulation of lesions at the molecular level[127]. It is implied that the accumulation of lesions embraces all cell structures without exception, ranging from the genetic material to membrane lipids. Arguments in

support of this hypothesis are examined in detail in previous Sections of this review. It would appear that agreement with this thesis logically requires the recognition of the universality of the action of antioxidants, which, by reducing the background level of the free radical reactions in the cell, decrease the number of stochastic lesions in biostructures. However, this simple treatment conflicts with facts: not all the antioxidants tested experimentally proved to be geroprotectants and the latter are in their turn active only in relation to specific objects. Thus according to Harman[128], 2-mercaptoethylamine, which has been tested on four strains of mice, increased by 29% the average lifespan of LAF_1 mice, but was almost inactive in relation to the AKR, Swiss, and C3H strains. The antioxidant 2,6-di-t-butyl-4-methylphenol (ionol or BHT) showed no influence on the rate of ageing of C57BL mice, but greatly increased the average lifespan of the BALB/C strain of mice[129,130]; the authors of both studies emphasise that the animals were maintained under optimum conditions. The geroprotectant 2-ethyl-3-hydroxy-6-methylpyridine hydrochloride retarded the rate of ageing of SHK at C3HA mice by a factor of 1.5–1.8. SHK mice belong to a non-inbred population characterised by a high incidence (50–90%) of spontaneous cancer of the mammary gland; the administration of this compound to mice of the AKR strain affected by spontaneous leukaemia was unsuccessful[131]. No attention has been devoted to the specific causes of the non-reproducibility of the results in the gerontological literature, it being merely stated that the given compound is active or inactive. This reflects the predominantly empirical approach to the problem. As a rule, in communications dealing with the retardation of ageing by chemical agents no well-founded methods for the selection of the dose of the preparation used in chronic experiments on survival are described; at best a preliminary study is made of toxic properties. As regards the selection of the dose of synthetic antioxidants, account must be taken primarily of their interaction with natural antioxidants, which can lead to the inhibition of stochastic free radical processes and to an increase of the reliability of the protecting systems of the organism or, conversely, it can induce the activation of peroxide oxidation and rapid depletion of the tissues in antioxidants[64]. It has been shown[86] that the range of doses of 2-ethyl-3-hydroxy-6-methylpyridine suitable for chronic experiments on laboratory mice is from 75 to 300 mg per kilogram of live weight. The use of this synthetic antioxidant in such amounts during the life of the animal makes it possible to maintain the antioxidant activity of the lipids (it is proportional to the content of the antioxidants in the tissues) above the normal level and to compensate for the age-induced decrease in the amount of natural antioxidants. The effectiveness of 2-ethyl-3-hydroxy-6-methylpyridine as regards the retardation of the ageing of Drosophila depends not only on its concentration but also on the stage of development, the age of the imago, sex, and the particular strain of the insects. In particular, it has been found that males are more sensitive to the geroprotectant than females; in experiments with females an increase of only the average lifespan was observed, while in the experimental groups of males the maximum lifespan also increased. The effect of this geroprotectant on flies of the $R(1)2yv/y^+Y$ strain with a rearranged karyotype also differed significantly from its effect on the D-32 wild strain. The average and maximum lifespan of males of the $R(1)2yv/y^+Y$ strain increased by 20% at a concentration of the preparation of 0.1 wt.%, whereas for the males of the D-32 strain this concentration of the preparation had the opposite effect: the rate of ageing increased and the lifespan diminished by 30%.[132] The decrease of the lifespan of guinea pigs observed when vitamin C was used in doses exceeding severalfold the physiological dose can be accounted for by the activation of the free-radical oxidation of lipids[133].

It is known that constant addition of certain chemicals to the diet can influence the consumption of food. This important aspect of the action of geroprotectants has been very little investigated. The influence of the antioxidant ionol on the appetite and live weight of adult rats is ambiguous and depends both on the concentration of the additive and on the composition of the food. The weight of the animals increased with increase of the concentration of ionol in the food up to 0.5% and remained constant when its content was raised to 0.9%, after which its slow decrease was observed. If the food contained at least 13% of protein, then the permissible dose of the antioxidant was 300 mg per kilogram of live weight per day; an increase of the protein content by a factor of two correspondingly made it possible to increase the safe dose of ionol[134]. Thus the application of the same chemical agent in different doses and for a variable diet may lead to opposite results even in the same species of animals.

Biological systems of different degrees of complexity, ranging from cell cultures to mammals, have been used as models in experimental gerontology. The more complex the system, the more stringent the requirements imposed on the potential geroprotectants, which must not interfere grossly in the metabolism and must not affect the course of the normal physiological processes. Hydrocortisone, which is a cell division stimulator, maintains active proliferation in old cell cultures, i.e. is a geroprotectant of the ageing of cultured cells in the given instance[135]. The properties of stabilisers of biomembranes make it possible to employ corticosteroids to retard the ageing of insects[136], whose tissues consist mainly of populations of non-dividing cells, in which the specific activity of lysosomal enzymes increases by a factor of 4–23 with increase of age[137]. However, the results of Akif'ev et al.[138] justify the rejection of corticosteroids as geroprotectants for mammals. The authors showed that constant stimulation of liver cells by hydrocortisone has a negative effect and leads to the breakdown of genetic regulation. Only instances of substitutional therapy are exceptions when hormones are used: the lifespan of dwarf mice increases under the influence of the growth hormone[139]; the ageing of autoimmune mice is retarded by prednisolone and hydrocortisone[140].

Vitamin E has been used successfully to retard the ageing of cultured diploid human fibroblasts and also increased the lifespan of Drosophila and nematodes[141,142]; however, numerous attempts to retard the ageing of laboratory mice demonstrated either a very low effectiveness of tocopherol or the complete absence of its influence on the rate of ageing. Nevertheless, vitamin E has a set of properties similar to those of synthetic antioxidants, namely ionol and santoquin (there is also a structural similarity with the latter), which may determine the geroprotecting activity or may accompany it[119]. It is still unknown why synthetic antioxidants have a more effective influence on the ageing of mammals than natural antioxidants. Presumably, when the physiological level of tocopherol or ascorbate is exceeded, the equilibrium involving the vitamins in the organism is disturbed[143]. Furthermore, it has been suggested that the function of vitamin E does not reduce exclusively to the antiradical activity[144].

The results of a study which established a decrease of the age-induced mortality of mice of the Swiss strain born to mothers which received the following antioxidants in their diet are very interesting and difficult to explain[145]: 0.2% of santoquin; 0.5% of 2-mercaptoethylamine; 0.2% of vitamin

E; 1% of sodium hypophosphite; a mixture of 0.2% of santoquin and 1.0% of sodium hypophosphite. The offspring were maintained on a constant diet without extraneous additives. At the age of 26 months, the fraction of surviving males whose mothers consumed 2-mercaptoethylamine and hypophosphite exceeded the control by 26 and 8%; santoquin and 2-mercaptoethylamine decreased the mortality of males by 13 and 23%. Vitamin E was inactive. The interpretation of this result is difficult, because the communication gives no information concerning any physiological or biochemical peculiarities of the offspring. It may be that the phenomenon of enzymatic imprinting, in which the administration of xenobiotics or other gene inductors to newborn animals induces in the latter a stable (over a period of 8 months and more) enhancement of adaptive synthesis, may be reflected in this instance in an unusual manner. Thus there is a phenotype correction of the symptoms of certain hereditary diseases. In 1974 attention was drawn to the fact that effective geroprotectants are as a rule inductors of microsomal oxidases[116]. The induction of the enzyme detoxification system of microsomes constitutes the molecular mechanism of the mobilisation of the protecting forces of the organism against the harmful influence of the chemical components of the environment and is manifested particularly clearly in chemical carcinogenesis, in which antioxidant inductors decrease the number of tumours or prevent their formation[147,148].

The results of several studies of the influence of antioxidants on the ageing of Drosophila showed that the most important events determining the lifespan occur in early ontogenesis. Using 2-ethyl-3-hydroxy-6-methylpyridine hydrochloride as the geroprotectant, it has been established[132] that the retardation of the ageing of Drosophila observed in this instance is not a consequence of the increase in the period of development. In addition it was found that the greatest effect is attained on treatment in the preimago stage or of the young imago, i.e. during the period when the phenotype characteristics of ageing are still absent. The older the imago, the less effective the geroprotectant: treatment begun at the age of 20 days and later is virtually without results. It has been suggested that lesions leading subsequently to ageing accumulate in the tissues of the larva from which the organs of the adult flies are formed (nervous tissue, imaginal discs). By regulating the incidence of these lesions in the larval period by means of a geroprotectant or a mutagen, it is possible to influence the rate of ageing of the adult individuals. According to the authors, the ageing of Drosophila consists of two stages: the stage of the accumulation of lesions and the stage of their realisation; the onset of the second stage requires not only a definite threshhold level of lesions but also a period of time after the elapse of which phenotype signs of ageing appear. Once this time has elapsed, a further increase in the number of lesions no longer has an appreciable influence on the rate of ageing. Since these stages are separated in time, it has been suggested that only molecules capable of prolonged storage of information about the harmful influence can serve as the "ageing substrate", i.e. the most likely candidate for the role of the ageing substrate is the molecule of chromosomal DNA. Information about the injury to other chemical components of the cell cannot be directly transmitted from the larvae to the adult individuals, since all the remaining components are repeatedly renewed in the course of metamorphosis.

The existence of a critical age limit beyond which treatment ceases to be effective or has the opposite result has been noted in a number of studies. In the investigation of the influence of α-tocopherylquinone on the ageing of a nematode, it has been observed[49] that the antioxidant is active only in relation to young animals; at the age of 20 days it was not possible to retard ageing. It may be that in the presence of an antioxidant the number of errors in the synthesis of membranes, which occurs most actively during the first ten days of the life of the nematode, is reduced[150]. Similar results have been published recently. The addition of lactic and gluconic acids to the feed of Drosophila larvae increased the average lifespan by 22%, while treatment of the young imagos was less effective by a factor of 2. The authors suggest that the retardation of ageing is achieved by inhibiting the reactions of the $OH^{\cdot}$ radical[120].

The causes of the existence of threshhold phenomena in ageing apparently involve the ratio of the rates of accumulation and repair of lesions. A mathematical treatment of a generalised scheme for the ageing process, taking into account critical phenomena, has been described[127].

The protecting effect of antioxidants in the age-induced accumulation of lesions of the secondary DNA structure is indicated by the results of Khudolii et al.[151] They established that lesions, recognised by endonuclease S_1 as apparently single-stranded breaks, accumulate during ageing in the mouse liver nuclear DNA. The retardation of the ageing of mice receiving an antioxidant is accompanied by a decrease of the number of similar defects.

The action of the majority of geroprotectants lacks a distinct specificity and is varied. The non-specific activity of antioxidants can be partly accounted for by their involvement in the reactions of the general adaptation syndrome, whose development occurs against the background of decreasing antioxidant activity of the tissues. In the state of stress, peroxide oxidation processes are activated[64]. Antioxidants modify the rate of supply of corticosteroids to the blood and lower the overall stress response. The prophylactic administration of antioxidants promotes adaptation under the conditions of experimental stress[152].

Studies in recent years established that antioxidants belong to the category of immunoactive compounds. The maximum humoral response of mice whose diet was permanently treated with antioxidants (vitamin E, ionol, santoquin, 2-mercaptoethylamine, etc.) corresponded to the age of 50–65 weeks and exceeded the control values approximately by a factor of 2. The cell immune response was enhanced to a lesser extent. It is believed[153] that life is prolonged because the age-induced immune deficiency is made good with the aid of antioxidants. A more careful examination of the results of this study makes it impossible to agree with this conclusion, since stimulation is replaced by immunodepression, which actually occurs in the experimental groups before the age-induced decrease of the immune response. This group of long-lived mice, whose life is prolonged as a result of a decrease of their mortality rate, reach the normal lifespan when the immune status is reduced. The retardation by antioxidants of the development of amyloidosis, a typical senile disease of the autoimmune type, can be logically explained by immunodepression[154]. The decrease of the rate of migration and proliferation of blood-forming stem cells in mice has been noted in chronic treatment with a geroprotectant belonging to the class of 3-hydroxypyridines. An increase by a factor of 1.5 of the latent period in the formation of spontaneous tumours of the mammary gland has been observed against the background of the immunodepression induced by the preparation[155]. The same preparation normalised the level of adrenalin in the adrenal gland of tumour carriers, which is believed[156] to be extremely significant for the outcome of the relations between the tumour and the organism.

The experimental data presented throw some light on the question why the action of antioxidants lacks a distinct specificity, depends on the complexity of the object, and is

frequently manifested by effects which are not clearly interrelated at first sight. Indeed, it is difficult to explain by a single cause data obtained for the same antioxidant and showing a decrease of the fraction of "defective protein" in liver cells[157] and a change of the rate of migration of blood-forming stem cells[155]. Although the hypothesis that geroprotectants act in both cases on the "membrane component" of ageing may be regarded as likely, a more exact answer requires a pharmacokinetic study of the preparation. Interference with the free radical oxidation reactions, which we believe constitute a universal background for metabolic processes, can be realised in accordance with the "weak link" principle and can lead to changes in a wide variety of biochemical mechanisms responsible for age-induced deviations. The structure and functional inter-relations between cells, tissues, and organs ensure the similarity of the final results of the age-induced changes due to different causes.

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Separation of Sulphur Isotopes by Physicochemical Methods

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Recent work on the separation of sulphur isotopes by distillation, chemical exchange, and isotope exchange methods is reviewed, and the characteristics of both laboratory and industrial apparatus for the separation of sulphur isotopes are tabulated. The direction of further developments is discussed with emphasis on a more rational organisation of the work and on the scientifically most promising approaches. 138 references.

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Natural sulphur is a mixture of stable isotopes of mass numbers 32, 33, 34, and 36, present at relative concentrations of 95.006, 0.76, 4.22, and 0.014 at.% respectively[1]. This isotopic composition is not absolute, and depends on the source of the sulphur, suggesting fractionation of the isotopes in the course of biochemical and geochemical processes. Fluctuations in the $^{32}S/^{33}S$, $^{32}S/^{34}S$, and $^{32}S/^{36}S$ isotope ratios can be as high as 2.5%, 5%, and 10% respectively[2,3]. The sulphur of the troilite in the Canyon Diablo meteorite, with an $^{32}S/^{34}S$ ratio of 22.22, has been adopted as the international standard[4].

Sulphur isotopes are used in biology[5,6], medicine[7], geology[8-16], nuclear physics[17,18], agrochemistry[20], organic[20-23] and physical chemistry[19,20,24-26], astronomy[27,28], physiology[29], etc.

Stable sulphur isotopes (and their methods of analysis) have also been used in practice to solve problems in geological uranium prospecting[30], estimating the quality of petroleum deposits[31], monitoring the sulphur content of cast iron and steel[20], and controlling the emission of sulphur waste gases and their rate of circulation and neutralisation in the atmosphere[32]. Another important group of applications of stable sulphur isotopes includes the preparation (by nuclear processes) of new radioactive isotopes, including the very important isotopes[17,18] ^{33}P and ^{35}S. The radioactive phosphorus isotope ^{33}P, prepared by the $^{33}S(n; p)^{33}P$ reaction, has been used increasingly in medicine and biology in recent years. Another radioactive isotope of phosphorus is known (^{32}P), but it is less easy to use in biochemical, ecological, agrochemical, and medical studies because its emission energy (E_{max} = 1.71 MeV) is higher than that of ^{33}P (E_{max} = 0.25 MeV).

It is clear, from recent publications, that the use of stable sulphur isotopes is increasing not only in the traditional branches of science and technology but also in new (and unexpected) directions. This explains the decision to create reserve stocks of these isotopes in many countries.

An analysis of the literature suggests that the three most important limiting factors to the still wider exploitation of stable sulphur isotopes are:

1) the high cost of these isotopes, due to the complexity of existing methods of production;

2) the complexity and high cost of the methods of isotopic analysis;

3) the lack of cheap, simple, and effective methods of synthesising the sulphur-labelled compounds needed in science and technology.

The most serious of these problems is the first. For example, the cost of one gramme of the ^{34}S isotope with an enrichment of 40–60 at.%, prepared by electromagnetic mass separation, is 4200 roubles, and the cost of one gramme of ^{36}S with an enrichment of 1.5–2 at.% is 50000 roubles[33]. The first paper dealing specifically with the technology of the separation of sulphur isotopes was published more than 40 years ago[34], and a great deal of work, both theoretical and practical, has been devoted to the separation problem throughout this period in many countries[25,29,35,36]. The development of new methods of separation stimulated the development of new or improved methods of analysis of sulphur isotopes[16,37-39], new methods of producing pure and specially pure sulphur, and new developments in the chemistry of labelled compounds[20-23].

The fact that according to papers published between 1937 and 1980 approximately 89 sulphur isotope separation processes were investigated in 46 scientific establishments of 13 countries gives an indication of the scale of this work. These developments have created a need for a systematic analysis of the different trends in the theory and practice of sulphur isotope separation, including an assessment of the factors which determine the cost of the isotopes, aimed at identifying promising directions in the search for cheaper isotopes. This review is devoted to these problems.

II. DISTILLATION

Processes based on the distillation of hydrogen sulphide, sulphur dioxide, and sulphur trioxide have been proposed for the separation of the sulphur isotopes. The choice of these compounds was dictated not only by general considerations of ease of distillation (simple apparatus design, easy and cheap flow reversal arrangements at the ends of the cascade, absence of side-processes leading to "parasitic" take-off), but also by the wide use of these compounds in the chemical industry. The latter circumstance offers a routine basis for the production of isotopes as well as the possibility of exploiting "transit" schemes, in which an existing industrial production flow of sulphur compound is used for the extraction of the heavy sulphur isotopes. The waste flow, with a decreased content of heavy sulphur isotopes, is returned to the chemical production cycle from which it had been diverted. In this way the intrinsic cost of the product can be lowered very substantially, and the problems of environmental protection can be greatly simplified, since the waste from the isotope production process is fully utilised elsewhere. We should stress that "transit" schemes are economically attractive not only in the extraction of isotopes by distillation but in any large-scale method of isotope production[40].

The results of a study of isotope equilibria in liquid–vapour systems are summarised in Table 1. We note that the use of SO_2 or SO_3 is unattractive because the separation coefficients (α) are extremely low: these coefficients effectively determine both the capital costs and the running costs of the process [since the size of the apparatus is specified by the expression $V \propto 1/(\alpha - 1)^2$, and the energy needed for phase reversal is $E \propto 1/(\alpha - 1)$], and they also control the length of the start-up time [$\tau \propto 1/(\alpha - 1)^2$].

Table 1. Separation coefficients for liquid–vapour phase equilibrium.

T, K	α	Method	Refs.	T, K	α	Method	Refs.
	$H_2{}^{32}S—H_2{}^{35}S$				$^{32}SO_2—^{35}SO_2$		
197	1.0053±0.0017	1	[51]	238	1.0018±0.0005	1	[51]
208	1.0058±0.0020	1	[51]	250	1.0030±0.0016	1	[51]
	$H_2{}^{32}S—H_2{}^{34}S$				$^{32}SO_2—^{34}SO_2$		
197	1.0035	2	[51]	238	1.0012	2	[51]
208	1.0038	2	[51]	261	1	3*	[53]
213	1.001÷1.0008	3*	[53]	298	1.0012	4	[47]
298	1.0023	4	[47]		$^{32}SO_3—^{34}SO_3$		
194.4	1.0023	1	[41]	317	1.001	3**	[54]
195.5	1.0034	1	[41]				
203.6	1.0048	1	[41]				
205.6	1.0054	1	[41]				
207.5	1.0067	1	[41]				

Symbols: methods of determining α: 1) simple distillation and calculation by the Rayleigh integral equation; 2) recalculation from the experimental values of $\alpha(^{32}S/^{35}S)$ obtained by method 1; 3) from the separation (K^∞) obtained in a column of height H_K having a known number of separation steps (n); 4) calculated by the equation

$$\varepsilon=(\alpha-1)=0.2\left(\frac{\Delta V}{\Delta T d}\right)^2\cdot\left\{1-\left[0.2\left(\frac{\Delta V}{\Delta T d}\right)^2\right]^2\right\}\cdot\left(\frac{T_{cr}}{T_{nbp}}-1\right)\cdot\varepsilon_K\Delta m,$$

where $\varepsilon_K = \frac{3}{2}\cdot\frac{1}{M}$ for mono-atomic molecules and

$$\varepsilon_K=\frac{3}{2}\cdot\frac{1}{M}+\frac{\mu}{m^3};$$

for polyatomic molecules, M is the molecular weight, μ is the reduced mass, $\Delta V/\Delta T = (V_{cr} - V_l)/(T_{cr} - T_{nbp})$, V_{cr} is the critical volume, V_l is the volume of the liquid at the normal boiling point, T_{cr} is the critical temperature, T_{nbp} is the normal boiling point, d is the density of the liquid, and Δm is the difference in mass between the isotopic molecules.

*H_K = 1 m; n = 96 ($^{10}BF_3$ – $^{11}BF_3$).
**H_K = 0.74 m; K^∞ = 1.022.

However, we should also note that though the data in Table 1 on the temperature dependence of α during the distillation of H_2S suggest relatively high values of the separation coefficient they include some inconsistencies, and a critical reappraisal of these results is essential. The simple distillation method[41,50] followed by calculation of α by the Rayleigh integral equation assumes that the initial hydrogen sulphide is free from involatile impurities, and that equilibrium conditions are maintained throughout the evaporation of the liquid phase[42–46]. Neither of these assumptions is invariably obeyed[42,44]. Results obtained from the distillation of H_2S in a column with a known number of theoretical plates (n) are also not entirely reliable, because the n values (determined for the distillation of BF_3) may not be exactly applicable to the distillation of H_2S. The determination of $\alpha(^{32}S/^{34}S)$ by calculation from experimental values of $\alpha(^{32}S/^{35}S)$ is also inexact, since it assumes that the separation coefficient is proportional to the relative difference in mass of the isotopic molecules.

In spite of these shortcomings of the methods the α values for low temperatures agree tolerably well (but not those for high temperatures). For example, the parameter $\varepsilon = (\alpha - 1)$ determined[51] at 208 K differs by a factor of 1.76 from the value obtained[41] by simple distillation followed by application of the Rayleigh integral equation, whereas the values of ε obtained[47,53] at 213 and 298 K respectively are 3–7 times lower than the values expected from the temperature dependence of α given in Ref. 41. We should also stress that the experimental results[41] are inconsistent with a quantum-statistical calculation[48] based on spectroscopic data. The latter discrepancy probably arises from failure to allow, in the calculation, for the complex composition of the liquid phase [including associated groups of the $(H_2S)_n$ type[49,50]].

Table 2. Results obtained for the separation of sulphur isotopes in fractionating columns*.

Specific load, kg S m^{-2} s^{-1}	HETP, cm	n	T, K	K^∞	Refs.
		$H_2{}^{32}S—H_2{}^{34}S$			
71.5	—	—	213	1.100	[53]
81.5	—	—		1.085	[53]
117.5	—	—		1.072	[53]
163.0	—	—		1.062	[53]
		$H_2{}^{32}S—H_2{}^{35}S$			
0.075	2.0	51	195	1.3÷1.38	[51]
		$^{32}SO_2—^{34}SO_2$			
55.5÷16.5	—	96—72**	—	***	[53]
		$^{32}SO_2—^{35}SO_2$			
0.0015	1.0	102	248÷255	1.23	[51]

*The separation reported in Ref. 51 was in a column of height H_K = 1.02 m and diameter D_K = 12 mm, packed with Nichrome spirals (1.5 × 1.5 × 0.2 mm). The separation reported in Ref. 53 was for a column having H_K = 1.0 m and D_K = 7.6 mm and packed with Constantan rings (1.2 × 0.25 mm).
**Estimated for the distillation of BF_3 from the degree of separation of $^{10}BF_3$ and $^{11}BF_3$.
***No separation detectable within experimental error.

The characteristics of the experimental assemblies used to study the separation of sulphur isotopes by distillation are listed in Table 2: the most favourable are those for the distillation of hydrogen sulphide, offering low values of the HETP (height of the equivalent theoretical plate) as well as the possibility of achieving high specific loadings. By using the criterion W to characterise the effectiveness of unit length of the column ($W = \ln K^\infty \cdot \tau/L$, where K^∞ is the stationary separation obtained in the column, τ is the transfer of the desired isotope along the column, and L is the flow circulating in the column) Devyatykh and co-workers[51] compared the effectiveness of various sulphur isotope separation processes. The conclusion was that hydrogen sulphide is

the best working substance for the separation of sulphur isotopes by distillation ($W_{H_2S} = 1.00$, $W_{SO_2} = 0.33$†), since its molecular weight is close to the atomic weight of sulphur, and it is a naturally occurring compound as well as being in industry on a large scale (for example, in the production of heavy water by the two-temperature hydrogen sulphide method[52]). The distillation of hydrogen sulphide could be of practical interest not only as a method of separation of sulphur isotopes but also in the production of very pure sulphur and sulphides[56], the demand for which has increased sharply in recent years.

An important contributory factor to the wide use of the hydrogen sulphide distillation process for the production of heavy sulphur isotopes is the amount of information already available on this process[41,51,55]. In addition to the above data on the isotope exchange equilibrium, wide-ranging results on the hydrodynamics of the distillation of hydrogen sulphide in glass columns under vacuum can be found in the published literature. This work has established that for the column packing used in the measurements [(2 × 2 × 0.3) × 10^{-3} m elements made of stainless steel wire and etched with a mixture of nitric and hydrochloric acid to improve the wetting] the maximum load L^* (kg m^{-2} h^{-1}) in the temperature range 189–210.6 K is described by the equation

$$L^* = -460 + 1870(d_e\gamma_v\gamma_l)^{0.5} \quad (1)$$

where d_e is the equivalent diameter of the packing (m), and γ_v and γ_l are the density of the vapour and of the liquid respectively (kg m^{-3}).

Experimental data on the retention capacity of the packing (ΔH) under the above conditions are described by the equation

$$\Delta H = 0.11\mathrm{Re}_l^{1/3}\left(a\frac{\mu_l}{\gamma_l}\right)^{2/3} \quad (2)$$

where μ_l is the viscosity of liquid H_2S, a is the specific surface area of the packing (in the present case, 3350 $m^2 m^{-3}$), and Re_l is the Reynolds number for the liquid phase.

The measurements of the hydraulic resistance of the packing are described by the equation

$$\frac{\Delta p}{l} = \lambda\left(\frac{W_v + W_l}{2g}\right)^2 \gamma_v \frac{a}{(V_{free} - \Delta H)^3} \quad (3)$$

where W_V and W_l are the linear velocities of the flows of vapour and liquid (m s^{-1}), λ is the coefficient of friction ($\lambda = 1600/\mathrm{Re}_V$), and V_{free} is the fractional free volume.

In conclusion we note that according to the reported[41] anomalous temperature dependence of α it should be possible to carry out the distillation of hydrogen sulphide without cooling: however, in view of the doubts mentioned above, this prediction requires experimental confirmation. We should also stress that because of the high toxicity of hydrogen sulphide the cost advantage of distillation under pressure may be offset by the more stringent requirements of completely leak-free operation.

To conclude this survey of distillation processes for the separation of sulphur isotopes we should not that the technological advantages of the distillation of H_2S mentioned above may rule out the use of any other compounds, in view of the steep increase in the demand for the heavy isotope ^{34}S (now more than 10 kg per annum) in a highly enriched state (≥90%).

†At the normal boiling point of the sulphur compound.

III. CHEMICAL ISOTOPE EXCHANGE

Chemical isotope exchange processes offer values of α much greater than those found in distillation, and are widely used in the production of isotopes of the lighter elements[40,57–60]. They also play a key role in the production of the heavy sulphur isotopes[35]. A large fund of experimental information on the equilibrium and kinetics of the isotope exchange of sulphur in chemical isotope exchange processes has accumulated during the past 40 years, and furthermore the technological value of the methods has been fully characterised.

The term technological value denotes the combination of factors not directly related to the isotope exchange process in the two-phase system and yet relevant to the technology and the economics of the separation process. The latter aspects can be predominant in determining the industrial importance of a process. These factors include the availability, compatibility, toxicity, and corrosion activity of the working substances, the problems arising in organising a continuous countercurrent process, the simplicity of the phase reversal arrangements, the cost of the processes involved, the possibility of combining the isotope separation process with other industrial operations, etc.

Table 3. Data on the isotopic equilibrium of sulphur in chemical isotope exchange processes.

T, K	$10^{-5}p$, Pa	Concentration of liquid phase	$\alpha(K)$ *	Method	Refs.
		$^{34}SO_2$—$H_2{}^{32}SO_4$			
478	1	—	1.0144(1.0176)	5 (6)	[63]
573	1	—	1.0108(1.0118)	5 (6)	[63]
673	1	—	1.0088(1.0088)	5 (6)	[63]
		$^{34}SO_2$—$NaH^{32}SO_3$			
293	0.403	1.445 M $NaHSO_3$	1.0155	7*	[65]
293	0.426	1.750 M $NaHSO_3$	1.0137	7*	[65]
293	0.401	1.445 M $NaHSO_3$	1.0103	7*	[65]
293	0.975	1.503 M $NaHSO_3$	1.0150	7*	[65]
323	0.974	1.656 M $NaHSO_3$	1.0136	7*	[65]
298	1	—	1.017	5	[66]
323	1	—	1.012	5	[66]
343	1	—	1.011	5	[66]
298	1	—	1.019(1.019)	—	[64, 67]
298	0.395	$NaHSO_3$ (sat.)	1.0181	1	[68]
308	0.395	$NaHSO_3$ (sat.)	1.0170÷1.0214	1	[68]
298	0.329	—	1.010÷1.015	8	[69, 70, 71]
298	1	1 M $NaHSO_3$	1.0109	1	[72]
308	1	1 M $NaHSO_3$	1.0110	1	[72]
318	1	1 M $NaHSO_3$	1.0113	1	[72]
298	1	—	1.0110	9	[73]
308	1	—	1.0090	9	[73]
318	1	—	1.0084	9	[73]
298	1	—	1.019	5	[74]
298	1	3 M $NaHSO_3$	1.016÷1.018	5	[75]
323	1	3 M $NaHSO_3$	1.012÷1.013	5	[75]
343	1	3 M $NaHSO_3$	1.010÷1.011	5	[75]
293	1	—	1.007	—	[76]
		$^{35}SO_2$—$NaH^{32}SO_3$			
298	1	1.3 M $NaHSO_3$	1.031	10	[77]
		$^{33}SO_2$—$NaH^{32}SO_3$			
343	1	3.0 M $NaHSO_3$	1.006	3**	[75, 76]
		$^{36}SO_2$—$NaH^{32}SO_3$			
298	1	—	1.043	—	[64, 74]
343	1	3.0 M $NaHSO_3$	1.022	3**	[75, 66]
		$^{34}SO_2$—$NH_4H^{32}SO_3$			
296	1	1.5 mole SO_2 $litre^{-1}$	1.005	5	[78]
295	1	5.1 mole SO_2 $litre^{-1}$	1.0075÷1.0080	5.7	[78]
293	1	6.9 mole SO_2 $litre^{-1}$	1.0095	5	[78]
293	1	10.2 mole SO_2 $litre^{-1}$	1.0130	5	[78]
353	1	0.95 mole SO_2 $litre^{-1}$	1.0025	5	[78]
353	1	2.90 mole SO_2 $litre^{-1}$	1.0070	5	[78]
353	1	9.90 mole SO_2 $litre^{-1}$	1.0070	5	[78]
		$H_2{}^{34}S$—$NaH^{33}S$			
303	1	—	****	3***	[79]

Table 3 (contd.).

T, K	10^{-5} p, Pa	Concentration of liquid phase	$\alpha(K)$ *	Method	Refs.
		$^{34}SO_2$—$H_2{}^{32}SO_3$ *****			
303	1	—	******	3***	[79]
298	1	0.081	1.0013	1	[80]
298	1	0.116	1.0021	1	[80]
298	1	0.182	1.0032	1	[80]
298	1	2.228	1.0035	1	[80]
298	1	0.390	1.0040	1	[80]
298	1	0.523	1.0047	1	[80]
298	1	0.661	1.0066	1	[80]
298	1	0.854	1.0090	1	[80]
308	1	0.026	1.0007	1	[80]
308	1	0.078	1.0021	1	[80]
308	1	0.254	1.0030	1	[80]
		$^{34}SO_2$—$H_2{}^{32}SO_3$ *****			
308	1	0.342	1.0034	1	[80]
308	1	0.744	1.0071	1	[80]
308	1	0.837	1.0084	1	[80]
318	1	0.127	1.0018	1	[80]
318	1	0.257	1.0036	1	[80]
318	1	0.571	1.0054	1	[80]
318	1	0.907	1.0087	1	[80]
303	1	0.620	1.0050	1	[80]

Symbols: K is the equilibrium constant; methods of determining $\alpha(K)$: 5) single equilibration, 6) calculated from spectroscopic data, 7) from the kinetic curve for the accumulation of product in the column, 8) from the amount of transport in the column, 9) calculated from the experimentally determined effective separation coefficients, 10) calculated as the arithmetic mean of $\alpha(^{32}S/^{34}S)$ and $\alpha(^{32}S/^{36}S)$; other symbols as in Table 1.

*H_K = 19.2 m; D_K = 50.8 mm.
**H_K = 1.0 m; D_K = 20 mm; n = 34.
***H_K = 1.8 m.
****Separation observed, but α not measured.
*****For this system the total concentration of sulphur in solution is given (calculated as SO_2).
******No separation.

The ratios of partition functions (β-factors) have been calculated[61,62,85] by inserting spectroscopic data into a model for many isotopically substituted sulphur-containing molecules and ions, and the equilibrium constants of the isotope exchange reactions of inorganic sulphur compounds have been obtained. By combining these results with experimental studies of sulphur isotope exchange equilibria (see Tables 3 and 4) and with phase equilibrium data we can identify and characterise a number of special features of the parameter α. The recognition of correlations in isotope effects in different systems can be useful not only in a rational search for the most effective working substances but also in optimising existing separation processes. However, we should note that many of the working systems listed in Refs.61 and 85 and in Tables 3 and 4 cannot be used in controlled sulphur isotope separation processes for a number of reasons (low rate of isotope exchange (see Table 5), low single-pass isotope effect, or difficulty in arranging the phase reversal at the ends of the separation cascade).

1. Hydrogen Sulphite Process

The hydrogen sulphite process, which relies on isotope exchange between gaseous SO_2 and the hydrogen sulphite ion HSO_3^-, satisfies most of the above requirements[35,60,75,78]. The slight discrepancies in the experimental values of α (Table 3) may be due to inadequacies in the methods employed or, in some cases, to failure to allow for the presence of other ions (e.g. SO_3^{2-} and $S_2O_5^{2-}$) in an aqueous solution of hydrogen sulphites containing dissolved SO_2.[72,73,80] The relative contribution of these spurious reactions to the overall separation effect is determined by the factors which influence the equilibrium between the various ions in the liquid phase: temperature, pressure, concentration of hydrogen sulphite, and pH.

Table 4. Data on the isotopic equilibrium of sulphur in chemical isotope exchange processes between SO_2 and its complexes (p = 0.1 MPa).

Workings system	T, K	r	α	Method	Refs.	Notes
$^{33}SO_2$— xylidene ·$^{32}SO_2$*	293	1.2	1.008	11**	[81,82]	—
$^{34}SO_2$— xylidene ·$^{32}SO_2$*	293	—	1.008	11**	[81,82]	—
$^{33}SO_2$— dimethylaniline · ·$^{32}SO_2$	293	—	1.009	11***	[81,82]	—
$^{34}SO_2$— dimethylaniline · $^{32}SO_2$	293	—	1.013	11***	[81,82]	—
»	297	1.55	1.001	3	[54]	H_K=0.84 m; K^∞=1.013
$^{34}SO_2$— triethylaniline · ·$^{32}SO_2$	303	1.82	1.002	3	[54]	H_K=0.84 m; K^∞=1.022
$^{34}SO_2$— aniline ·$^{32}SO_2$	303	1.47	1.002	3	[54]	H_K=0.84 m; K^∞=1.028
$^{34}SO_2$— nitrobenzene · $^{32}SO_2$	303	—	****	3	79]	H_K=1.8 m
$^{34}SO_2$— methanol·$^{32}SO_2$	273	—	****	3	[79]	H_K=1.8 m
$^{34}SO_2$— $(CH_3CO)_2O$·$^{32}SO_2$	273	—	1.0005	—	[83]	—
$^{34}SO_2$—$B(OCH_3)_3$·$^{32}SO_2$	—	—	*****	—	[83]	—
$^{34}SO_2$—CH_3CN·$^{32}SO_2$	—	—	*****	—	[83]	—
$^{34}SO_2$— complex $^{32}SO_2$******	298	—	1.0022	—	[83]	—
$^{34}SO_2$— $H^{32}SO_3^-$	298	—	1.014	12	[47]	—
$^{36}SO_2$— $H^{32}SO_3^-$	298	—	1.028	12	[47]	—
$^{34}SO_2$—$(CH_3)_2O$·$^{32}SO_2$	273	58% SO_2 42% $(CH_3)_2O$	1.0005	3	[84]	n=15; K^∞=1.008
$^{34}SO_2$— pyridine ·$^{32}SO_2$	303	1.24	1.002	3	[54]	H_K=0.84 m; K^∞=1.027
$^{34}SO_2$— ethylene oxide · ·$^{32}SO_2$	288	0.6	1.000	3	[54]	H_K=0.84 m; K^∞=1.008
$^{34}SO_2$— thiophen $^{32}SO_2$	303	—	****	3	[54]	H_K=0.84 m;
$^{34}SO_2$— tetrahydrofuran ·$^{32}SO_2$	303	—	****	3	[54]	H_K=0.84 m;
$^{34}SO_2$— phenol·$^{32}SO_2$	303	—	****	3	[54]	H_K=0.84 m;
$H_2{}^{32}S$ — $H^{34}S^-$	298	—	1.003	12	[47]	—
$^{34}SO_2$—water·$^{32}SO_2$	298	—	****	3	[79]	H_K=1.8 m

Symbols: r is the composition of the complex (mole SO_2 mole^{-1} complex former). Methods of determining α: 11) repeated equilibration; 12) calculated by the equation

$$\varepsilon = (\alpha - 1) \simeq 0.7\, \varepsilon_\lambda \Delta m,$$

where

$$\varepsilon_\lambda = \left[\left(\frac{3}{2}\frac{1}{M_{AC}} + \frac{\mu_{AC}}{m^2}\right) - \left(\frac{3}{2}\frac{1}{M_{AB}} + \frac{\mu_{AB}}{m^2}\right)\right];$$

other symbols as in Tables 1 and 3.

*Xylidene diluted with water (1:2 ratio).
**Five-fold equilibration.
***Three-fold equilibration.
****No separation.
*****Separation observed, but α not measured.
******Complex of $^{32}SO_2$ with an azeotropic mixture of pyridine (43%) and water.

Many workers have studied the influence of these factors on the separation process (see Table 6): in most cases the measurements were made with aqueous solutions of sodium

or ammonium hydrogen sulphite[65,66,71,75,76,78,83,88,89]. The optimum conditions for the separation of the sulphur isotopes were found to be: temperature 343 K, concentration of hydrogen sulphite in solution 3–4 mole litre^{-1}, pressure ~0.03 MPa, and preferably using a solution of ammonium hydrogen sulphite.

Table 5. Studies of the rate of isotope exchange.

T, K	Experimental data: $10^{-3}t$, s	Experimental data: a, %	τ, s	References
		$^{32}SO_2$—$H^{35}SO_4^-$		
298	173	0	—	[86]
298	75.6	0	$>85\cdot10^7$	[86]
298	4920	$<0.4\pm0.1$	—	[86]
373	173	5	—	[86]
374	1200	1.6 ± 0.2	$\sim50.4\cdot10^6$	[86]
410	554	19 ± 0.3	$177.5\cdot10^4$	[86]
408	905	30.6 ± 0.4	—	[86]
433	25.2	3.8 ± 0.2	$53.6\cdot10^4$	[86]
433	188.5	18.8 ± 0.3	—	[86]
484	5.4	14.2 ± 0.2	$27\cdot10^3$	[86]
484	10.8	22.5 ± 0.3	—	[86]
553	<18	100	—	[86]
		$H^{35}S$—$^{32}S^{32}SO_3^{2-}$		
373	3.6	*	—	[87]
373	86.4	100	—	[87]
		$(HS^{33}S)=(H^{35}SS)^-$		
363÷373	3.6	100	—	[87]
		$^{35}SO_3^{2-}$—$^{32}S_2O_3^{2-}$		
293	72	0	—	[87]
330	3.6	*	—	[87]
330	75.6	100	—	[87]
373	3.6	100	—	[87]
		$^{32}S^-$—$^{35}SO_4^{2-}$		
373	129.6	**	—	[87]
		$^{32}SO_3^{2-}$—$^{35}SO_4^{2-}$		
373	129.6	**	—	[87]
373	126	**	—	[87]
		$^{32}SO_2$—$^{35}SO_3$		
553	61.2	**	—	[87]
608	86.4	*	—	[87, 86]
		$^{32}SO_2$—($^{35}SO_3+H_2O$)		
323	10.8	**	—	[87, 86]
		$^{32}SO_2$—($^{35}SO_3+{}^1/_3H_2O$)		
553	54.0	*	—	[87, 86]
		$^{32}SO_2$—($^{35}SO_3$+Pt on asbestos)		
553	14.4	*	—	[87, 86]
		$C^{32}S_2$—$H_2{}^{35}S$—N_2		
673	10.8	5÷6	—	[22]
		$C^{32}S_2$—[$Fe^{35}S$]***—N_2****		
473	—	1	—	[22]
573	—	11÷13	—	[22]
773	—	26	—	[22]
673	$10\cdot10^{-3}$	100	—	[22]
		$H_2{}^{32}S$—[$Fe^{35}S$]***—N_2****		
473	—	2.2	—	[22]
573	—	26.0	—	[22]
673	—	73.0	—	[22]
673	*****	100.0	—	[22]
		$CO^{32}S$—[$Fe^{35}S$]—N_2******		
473	—	13	—	[22]

Table 5 (contd.)

T, K	Experimental data: $10^{-3}t$, s	Experimental data: a, %	τ, s	References
		$C_4H_4{}^{32}S$—[$Fe^{35}S$]—N_2******		
473	—	0	—	[22]
573	—	1	—	[22]
673	—	15	—	[22]
723	—	27	—	[22]

Symbols: t is the duration of the experiment, a is the fractional amount of exchange, τ is time of half-exchange.

*Partial exchange.
**No exchange.
***[$Fe^{35}S$] is a sulphidised nickel–chromium catalyst of composition 87.95% Fe_2O_3, 7.9% CO_3^{2-}, 3.66% SO_4^{2-}, 0.31% CaO, 0.18% MgO.
****Experiments under dynamic conditions, with a volume feed rate of the gas mixture of 1200 h^{-1}.
*****Several seconds.
******Experiments under static conditions.

Solutions of sodium or ammonium hydrogen sulphite were found to be prone to "ageing" effects[65,71,75] associated with oxidation by dissolved atmospheric oxygen in the presence of ultraviolet light. It was noted[89] that the "ageing" of hydrogen sulphites takes place in two steps: in the first, sulphate, thiosulphate, and polythionates are formed, and in the second the thiosulphate and polythionates are converted into sulphate and free sulphur (generating small quantities of sulphate). The solution develops a colour, due to colloidal sulphur. The formation of colloidal sulphur takes place mainly by the reaction

$$S_2O_3^{2-} + 2H^+ \rightleftarrows H_2S_2O_3 \rightleftarrows H_2O + SO_2 + S$$

in the reactor of the lower flow reversal unit, in parallel with the decomposition of the hydrogen sulphite by sulphuric acid at $T \cong 373$ K. All these side-reactions in the solution of hydrogen sulphite should, in principle, disturb the technological regime and cause a loss of enriched product, since the exchange between HSO_3^-, SO_3^{2-}, and SO_4^{2-} ions is negligible both in acid and in alkaline solutions (as is also the exchange between thiosulphates, polythionates, and colloidal sulphur).

Many attempts to "moderate" the ageing of hydrogen sulphite solutions by various means have been reported, including additions of oxidation inhibitors, degassing of the solutions, improved designs of the lower flow reversal unit, and a search for an oxidation-resistant source of hydrogen sulphite ions. It was found that small amounts of hydroquinone[68] or *N*,*N*-dimethylformamide[80] can be used as oxidation inhibitors in solutions of ammonium hydrogen sulphite. Auto-oxidation was also shown to be avoidable[65] by degassing the initial solutions and by displacing the air in the column with an inert gas.

Many workers have found that the oxidation of hydrogen sulphite depends on the method of preparation of the solutions[75] and on their purity[71]. Thus the formation of colloidal sulphur can be largely suppressed by using freshly prepared solutions of sodium hydrogen sulphite[75]. A comparative study of different sources of hydrogen sulphite ions ($NaHSO_3$, $KHSO_3$, NH_4HSO_3, $Na_2S_2O_5$) showed that industrially the best results are obtained with sodium pyrosulphite[90] supplied in a crystalline form, which allows solutions of $Na_2S_2O_5$ to be

Table 6. Separation of sulphur isotopes in chemical isotope exchange processes.

n_{st}	N *	Shape, material, and size of packing	H_K, m	D_K, mm	c	10^4 G, $m^3\ m^{-2}\ s^{-1}$	HETP, cm	T, K	$-p$, MPa	K^{∞} (Y^{∞})	w, kg $^{34}S\ s^{-1}$	Refs.
					$^{32}SO_2$—$NaH^{34}SO_3$							
1	5×4.5	ceramic saddles, 6 mm	24	70	3.2 M	1.13	—	298	0.0329	(8% ^{34}S)	$3.70\cdot10^{-8}$	[67], [71]
2	3×4	glass Fenske helices, 6 mm	12	22	3.2 M	4.38	—	298	—	(15% ^{34}S)		
3	1×4.5; 1×3.0	glass Fenske helices, 6 mm	7.5	10	3.2 M	5.51	—	298	—	(27% ^{34}S) **		
1	1	spirals of Kh18N10T stainless steel wire, 1.8 × 1.6 × 0.2 mm	1.0	20	3.0 M	1.665	9.6	298	0.1	1.19	—	[75]
					3.0 M	1.665	3.6	333	0.1	1.36		
					3.0 M	1.665	2.9	343	0.1	1.45		
					3.0 M	1.665	3.3	353	0.1	1.40		
					4.0 M	1.665	4.4	333	0.1	1.31		
					4.0 M	1.665	2.9	343	0.1	1.45		
					4.0 M	1.665	3.4	353	0.1	1.38		
1	1	ceramic Raschig rings, 6.3 mm	19.2	50.8	1.445 M	6.46	3.13	293	0.0487	1.32	—	[65]
					1.445 M	3.25	2.35	293	0.0401	1.35		
					1.503 M	4.91	3.68	293	0.0975	1.36		
					1.750 M	4.33	2.67	293	0.0426	1.321		
					1.635 M	4.96	2.21	323	0.0975	1.485		
1	1	circular spirals, 1.6 × 1.6 × 0.2 mm	0.5	20	1.0 M	1.85	—	293	0.1	1.098	—	[76]
					2.1 M	1.82	—	293	0.1	1.165		
					3.0 M	1.765	—	292.5	0.1	1.212		
					4.1 M	1.765	—	293	0.1	1.192		
					5.0 M	1.735	—	293	0.1	1.193		
					3.0 M	1.765	—	313.5	0.1	1.287		
					3.0 M	1.765	—	333	0.1	1.327		
					3.0 M	1.765	1.82	292.5	0.1	1.212		
					3.0 M	4.6	3.13	292.5	0.1	1.118		
					3.0 M	6.72	5.47	292.5	0.1	1.066		
1	1	—	20	12	—	—	—	—	—	***		[69]
					$^{32}SO_2$—$NaH^{35}SO_3$							
1	1	carbon, AG grade	3.0	13	0.558 N	—	—	298	0.1	1.089	$2.68\cdot10^{-7}$ ($K=1.203$)	[77]
					1.020 N	—	—	298	0.1	1.160		
					1.300 N	0.338	—	298	0.1	1.115		
					1.300 N	0.752	—	298	0.1	1.202		
					1.300 N	0.880	—	298	0.1	1.168		
					1.300 N	1.005	—	298	0.1	1.118		
					1.300 N	1.257	—	298	0.1	1.060		
					1.300 N	—	50	298	0.1	1.203		
					1.580 N	—	—	298	0.1	1.157		
					2.040 N	—	—	298	0.1	1.142		
					2.51 N	—	—	298	0.1	1.105		
					$^{32}SO_2$—$NH_4{}^{34}SO_3$							
1	1	circular spirals of stainless steel, 1.6 × 1.6 × 0.2 mm	0.5	20	1.3 M	1.85	—	292.5	0.1	1.21	—	[78]
					1.9 M	1.85	—	293	0.1	1.20		
					3.4 M	1.765	—	293	0.1	1.26		
					5.1 M	1.680	—	293	0.1	1.24		
					6.0 M	1.765	—	292.5	0.1	1.22		
					6.9 M	1.765	—	293.5	0.1	1.20		
					10.2 M	1.765	—	295	0.1	1.12		
					2.9 M	1.765	—	353	0.1	1.463		
					6.6 M	1.765	—	353	0.1	1.32		
					7.3 M	1.765	—	353	0.1	1.32		
					9.9 M	1.765	—	353	0.1	1.182		
					3.0 M	1.765	0.93	353	0.1	1.46		
					4.0 M	1.765	1.00	353	0.1	1.42		
					5.0 M	1.765	1.09	353	0.1	1.38		
					6.0 M	1.765	1.20	353	0.1	1.34		
					7.0 M	1.765	1.34	353	0.1	1.30		
					8.0 M	1.765	1.52	353	0.1	1.26		
					9.0 M	1.765	1.76	353	0.1	1.22		
					10.0 M	1.765	2.12	353	0.1	1.18		
					1.3 M	1.765	1.23	293	0.1	1.21		
					1.9 M	1.765	1.27	293	0.1	1.232		
					3.4 M	1.765	1.45	293	0.1	1.26		
					$^{32}SO_2$—$NH_4H^{34}SO_3$							
1	1	circular spirals of stainless steel, 1.6 × 1.6 × 0.2 mm	0.5	20	5.1 M	1.765	1.93	293	0.1	1.24	—	
					6.0 M	1.765	2.29	293	0.1	1.22		
					6.9 M	1.765	2.74	293	0.1	1.20		
					8.0 M	1.765	3.50	293	0.1	1.17		
					9.0 M	1.765	4.30	293	0.1	1.15		
					10.2 M	1.765	5.50	293	0.1	1.12		
1	1	circular spirals of wire, 1.6 × 1.6 × 0.2 mm	0.5	20	5.0 M	1.915	3.85	293	0.1	1.11	—	[88]
1	1	extended circular spirals of wire, 1.6 × 1.6 × 0.2 mm	—	20	5.0 M	1.93	1.72	293	0.1	1.275	—	[88]

Table 6 (contd.).

n_{st}	N*	Shape, material, and size of packing	H_K, m	D_K, mm	c	10^4 G, $m^3\ m^{-2}\ s^{-1}$	HETP, cm	T, K	p, MPa	K^{∞} (Y^{∞})	w, kg $^{34}S\ s^{-1}$	Refs.
1	1	triangular spirals of wire, 1.6 × 1.6 × 0.2	0.5	20	5.0 M	1.85	1.79	293	0.1	1.25	—	[88]
1	1	extended triangular spirals of wire, 1.6 × 1.6 × 0.2 mm	0.5	20	5.2 M	1.80	1.30	293	0.1	1.36	—	[88]
1	1	extended square spirals of wire, 1.6 × 1.6 × 0.2 mm	0.5	20	5.0 M	1.93	2.87	293	0.1	1.15	—	[88]
1	1	acid-resistant spirals No.316	3.0	40	3.0 M 3.0 M 3.0 M 3.0 M 3.0 M 3.0 M	0.833 1.665 2.500 1.665 0.833 1.665	5.50 10.00 13.00 5.10 1.44 3.30	298 298 298 322 343 343	0.1 0.1 0.1 0.1 0.1 0.1	a column 5.5 m high gave 100 litre of SO_2 containing 50 at.% ^{34}S		[29]
					$H_2{}^{32}S$—$NaH^{34}S$							
1	1	glass spirals	8.0	10	sat.soln.	—	—	298	0.1	1.063 (^{34}S becomes concentrated in the gas)		[79]
					$^{32}SO_2$—$Na_2{}^{34}S_2O_5$							
1	1	triangular spirals of stainless steel wire, 2.2 × 2.2 × 0.2 mm	8.0	27	3.0 *M*	3.50	6.4	343	0.1	—	—	[90]
2	1	triangular spirals of stainless steel wire, 1.8 × 1.6 × 0.2 mm	12.0	21	3.0 *M*	2.42	5.0	343	0.1	****	—	[90]

Symbols: N is the number of columns in the cascade step, n_{st} is the number of steps in the cascade, c is the concentration of hydrogen sulphite, G is the specific load, Y^{∞} is the stationary concentration, w is the output rate.

*The first figure is the number of columns, the second is the height of the columns in metres.
**Non-stationary concentration reached in ~18 × 10^5 s.
***Concentrations of 10.2% ^{34}S and 1.5% ^{33}S reached; non-stationary, though reached without take-off.
****Concentrations of 45% ^{34}S, 2.7% ^{33}S, and 0.9% ^{36}S reached.

prepared immediately before the separation process. Furthermore, by using a reactor incorporating three separately heated sections[75] and carrying out the lower phase reversal operation at successively higher temperatures (50, 75, 95, and 100–105 °C) the precipitation of colloidal sulphur was suppressed to a large extent and quantitative evolution of the SO_2 was obtained though its concentration in the effluent solution was very low (5 × 10^{-3} kg m^{-3}). Small amounts of colloidal sulphur were precipitated after lengthy boiling of the solutions, but they were easily entrained by the liquid and did not interfere with the separation.

An isotopic analysis of the colloidal sulphur precipitated during the separation was carried out[75] in order to determine whether the precipitation causes a loss of enriched product. Though the laboratory apparatus produced a concentration of ^{34}S of 6.2% at the lower end of the column in a stationary regime, the isotopic composition of the sulphur was identical to that of the initial solution, showing that the precipitation of colloidal sulphur had not caused a loss of enriched product. This conclusion is of the utmost importance in determining the possibility of obtaining sulphur isotopes at high concentrations by the hydrogen sulphite process, and it requires experimental confirmation by the same method but at higher levels of enrichment of ^{34}S in the column.

Another important series of studies on the hydrogen sulphite process was aimed at developing improved apparatus designs and lowering the unit cost of the process. Perhaps the most significant of these were the search for a more effective type of column packing[66,71,88] and the work on minimising the cost of flow reversal. The need for these improvements was dictated by the very high values of the HETP (from 0.25 to 1.1 m) reported in the early publications[65, 71,77] (see Table 6) and by the excessive consumption of relatively expensive high-purity reagents in the flow reversal process.

One of the earliest attempts[71] to increase the efficiency of the packing (by improving its wetting by the working solution) relied on the addition of small amounts of technical octanol, but the performance of the packing (glass saddles or Fenske helices) was not measurably improved. Nevertheless the use of additives to improve the wetting of the packing and to increase the rate of diffusion processes in the liquid phase should not be dismissed, especially if the additives also act as oxidation inhibitors for the hydrogen sulphite ions, if they assist the flow reversal or protect the apparatus from corrosion, or if they favour the mutual solubility of the phases participating in the separation. An alternative method of increasing the effectiveness of the

packing relies on etching the surface with acid solutions (in the case of stainless steel packings). This method is interesting, and its effectiveness has been noted in a number of studies of different isotopic mixtures using different packings[54,91,93].

The most systematic investigation of possible ways of improving the effectiveness of column packings for the hydrogen sulphite process was reported by Stiehl and coworkers[88]. By studying five types of stainless steel packing of different geometrical form they showed that the best packing consists of extended triangular spirals, which offer a large free volume and a low retention for aqueous solutions of hydrogen sulphites. These workers calculated that by using this type of packing for the separation of sulphur isotopes in the NH_4HSO_3–SO_2 system an apparatus not exceeding 35.4 m in height can give a fractional take-off of 90%-enriched ^{34}S equal to 0.2677×10^{-3} of the flow (L) circulating in the column. The calculations apply to an aqueous solution of NH_4HSO_3 with a total concentration of SO_2 of 9 mole litre^{-1}, assuming a working temperature of 353 K and a specific loading (with liquid) of 1.765×10^{-4} m^3 m^{-2} s^{-1}.

At the current level of production of sulphur isotopes (up to 2 kg of 50–90% ^{34}S per annum[90]) the most important item in the overall cost of manufacture is that of the flow reversal arrangements (in addition to the labour costs)[35].

One of the most promising methods of minimising this cost in the hydrogen sulphite process is to combine this separation with the separation of nitrogen isotopes in the NO–HNO_3 chemical exchange system[76] (see Fig.1)#, which can itself easily be combined with the low-temperature distillation of NO to yield oxygen isotopes[96]. A combination of these processes by the scheme shown in Fig.1 minimises the flow reversal costs of both the hydrogen sulphite and the HNO_3–NO process as well as solving the problem of by-product utilisation. Any practical embodiment of this scheme should include provisions for removing dissolved SO_2 from the sulphuric acid emerging from the lower flow reversal unit of the "nitric acid" assembly: otherwise, the acid will cause a serious dilution of the enriched sulphur isotopes when admitted to the lower flow reversal unit of the "hydrogen sulphite" assembly.

The problem of removing dissolved SO_2 from the sulphuric acid is made much simpler by organising the flow reversal in the NO–HNO_3 process as shown in Fig.2. This allows the concentration of the H_2SO_4 issuing from the flow reversal unit to reach 70–75% [100] (since the solubility of SO_2 in H_2SO_4 goes through a minimum as the concentration increases to 80% [99]). The concentration of SO_2 in the sulphuric acid is lowered also by heating the acid, since the solubility varies inversely with temperature. For example, according to standard Tables[98] the solubility of SO_2 in 95% H_2SO_4, which is 25 m^3 SO_2 m^{-3} H_2SO_4 at 298 K, falls to 4 m^3 SO_2 m^{-3} H_2SO_4 at 363 K. This suggests that failure to control the SO_2 content of the sulphuric acid used for flow reversal in "hydrogen sulphite" plants may be responsible for the reported[76,83] discrepancies in the HETP obtained for isotope exchange between the hydrogen sulphite ion and SO_2 in counter-current packed columns and in ion exchangers[17,101] (see also Tables 6 and 9). In the latter case the motion of the Spedding zone was achieved by using hydrochloric rather than sulphuric acid (thus avoiding the presence of dissolved SO_2). We also note from the results in Table 6 that substantially different values of the HETP were obtained by different workers using H_2SO_4 for flow reversal in counter-current columns under similar conditions (identical temperature, pressure, concentration of hydrogen sulphite ion, load (and shape and size) of the packing, and similar column diameters).

#The production of a kg of ^{15}N by the NO–HNO_3 process requires a supply of more than 50000 kg of sulphur dioxide for flow reversal[97]. This gas is a waste product in the hydrogen sulphite process, and at the same time the waste product of the NO–HNO_3 process (sulphuric acid) can be utilised (after suitable treatment) to induce flow reversal in the hydrogen sulphite process.

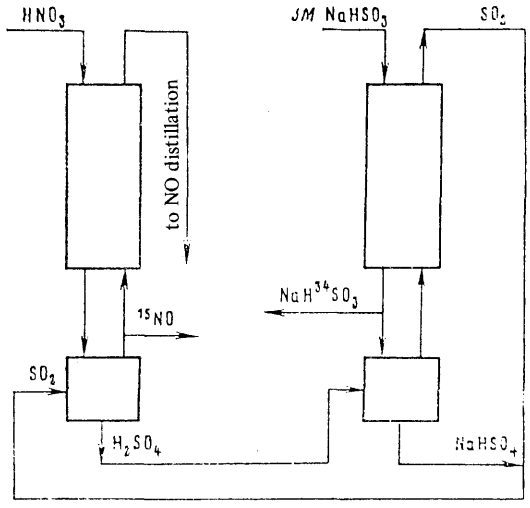


Figure 1. Combination of the hydrogen sulphite sulphur isotope separation and the NO–HNO_3 nitrogen isotope separation process.

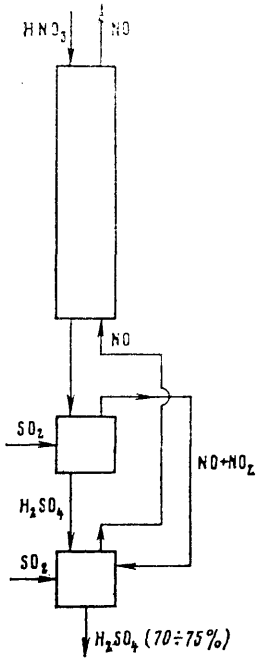


Figure 2. Flow reversal scheme suggested[100] for the lower unit in the nitrogen isotope separation process.

Knowing the maximum solubility of SO_2 in sulphuric acid[98] we can calculate the possible isotopic dilution of the product caused by the SO_2 of natural isotopic composition contained in the sulphuric acid added to the flow reversal unit. For a concentration of ^{34}S of 4.2 at.%, and a separation coefficient of the ^{32}S and ^{34}S of $\alpha = 1.008$ (at 20 °C), the production of 1 kg of ^{34}S in an apparatus without take-off requires the treatment of a flow of raw materials containing $L = p/x_0\Gamma \cong$ 3000 kg of sulphur, as well as an input of 9000 kg of H_2SO_4 for flow reversal. At 293 K the solubility of SO_2 is 0.0365 kg SO_2 kg^{-1} H_2SO_4, and as a result of isotopic dilution the ^{34}S content of the product may fall from $x_K = 100\%$ to $x_K = 4.79\%$. At higher temperatures the solubility of SO_2 decreases, but not to a negligibly low value. For example, at 90 °C the solubility is 0.00475 kg SO_2 kg^{-1} H_2SO_4, which can also lead to marked isotopic dilution ($x_K = 8.5\%$). Evidently, failure to allow for these effects may have been responsible for serious errors in the determination of the HETP from experimental values of the degree of separation obtained, and hence it may explain the large discrepancies between HETP values reported from different laboratories.

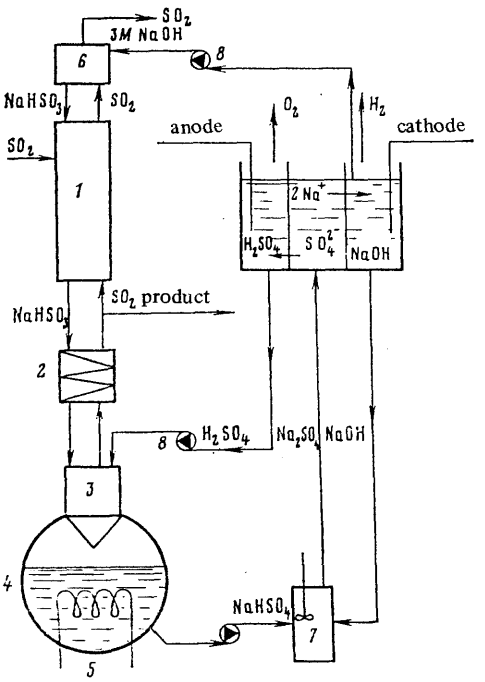


Figure 3. Flow reversal using an electro-dialysis system in the hydrogen sulphite process: *1*) exchange column, *2*) condenser, *3*) hydrogen sulphite decomposition column, *4*) boiler, *5*) heater, *6*) reactor of upper flow reversal unit, *7*) hydrogen sulphite converter, *8*) pump.

In order to reduce the cost of the reagents used for flow reversal (sulphuric acid in the lower unit and sodium hydroxide in the upper unit for flow reversal in a "hydrogen sulphite" apparatus with take-off) an electro-dialysis system has been used[19,25,35,36] to regenerate NaOH and H_2SO_4 from the $NaHSO_4$ formed in the lower flow reversal unit (Fig.3). The additional consumption of electrical energy in this case is 3500 kJ per mole of $NaHSO_4$.[35]

The advantages of the electro-dialysis scheme include inducing flow reversal by using electrical energy, and the possibility of using a gas as feed-stock (thus allowing the process to be combined with the "nitric acid" process, or, using the "transit" scheme, with the sulphuric acid process based on SO_2). Furthermore this scheme avoids the difficulties arising from the need to use freshly prepared solutions of hydrogen sulphite, and minimises "ageing" effects.

The problem of using HETP data obtained for small-diameter columns in the design of large industrial isotope separation plant is still unsolved. However, for the hydrogen sulphite process this problem is easily solved by using the abundant experimental information on HETP values available for columns of widely different diameter (up to 0.07 m [71]) and using packing of different shape and size (see Table 6).

We shall conclude this discussion of the hydrogen sulphite process with a brief review of the characteristics of industrial assemblies and of the results of experiments in large laboratory apparatus and in pilot plant. The first separation of sulphur isotopes by the hydrogen sulphite process was achieved in a fairly large laboratory cascade assembly[67,70,71] whose main parameters are listed in Table 6. Because of the low flow rate of gaseous SO_2 the pressure drop in the columns was also low, and therefore the cascade could be operated without intermediate gas compressors. A stationary distibution of ^{34}S concentration was reached after 21 days' operation of the cascade. It was found that 3.0×10^{-5} m^3 of enriched $NaHSO_3$ solution (3.2×10^{-3} kg of sulphur) could be taken daily from the last column of the cascade with a concentration of ^{34}S not less than 25%. Having determined experimentally the hold-up of ^{34}S in the column, Thode and co-workers[70] calculated the average rate of transfer (1.272×10^{-8} kg ^{34}S s^{-1}).

It was subsequently found[69] that the heavy sulphur isotopes could be concentrated to the level of 10 at.% ^{34}S and 1.5 at.% ^{33}S in the $NaHSO_3$–SO_2 system by using an apparatus with columns 20 m high. In the early 1970's a cascade consisting of two columns 8 and 12 m high was built in the Soviet Union, and this gave an enrichment of 45 at.% for ^{34}S, 2.7 at.% for ^{33}S, and 0.9 at.% for ^{36}S in 20 days. From these results a design was produced for a three-column cascade apparatus capable of producing 0.5 kg $year^{-1}$ of sulphur containing 90 at.% of ^{34}S or 0.1 kg $year^{-1}$ of sulphur containing 3 at.% of ^{36}S. The estimated cost[90] was 117000 roubles per kilogramme of ^{34}S and 580000 roubles per kilogramme of ^{36}S.

A group of French workers[29] described a series of tests on a large-scale apparatus consisting of a column 5.5 m long and 0.04 m in diameter filled with Helipak 316 packing. By using the NH_4HSO_3 system these workers studied the effect of load and temperature on the HETP at atmospheric pressure and 3 M concentration of the aqueous hydrogen sulphite solution. Their results are given in Table 6. A comparison of these results with those obtained[75] under otherwise similar conditions for the $NaHSO_3$–SO_2 system in a column 0.02 m in diameter confirms the report[76,102] that the HETP for the NH_4HSO_3–SO_2 system is lower than the corresponding value for the $NaHSO_3$–SO_2 system. These pilot experiments established that the apparatus can produce 0.1 m^3 day^{-1} of SO_2 containing 50% of ^{34}S.

The development of a large-scale apparatus for separating sulphur isotopes at the Mound laboratory (USA) has recently been described[25,35,36]. It is based on the laboratory's five-step cascade process for the production of carbon-13 by the amine–carbamate method[36,103]. The consumption of reagents for flow reversal is minimised by adopting an electro-dialysis system in conjunction with the $NaHSO_3$–SO_2 working system.

The separation is carried out at 343 K with a 3 M concentration of sodium hydrogen sulphite in water. For a feed rate of $(1.157–3.48) \times 10^{-5}$ kg SO_2 per day this plant is expected to produce 5×10^{-8} kg of ^{34}S with a concentration of 90 at.% per day at a cost between 100000 and 200000 dollars per kilogramme. It is also proposed[36] to use some of the product in the Mound laboratory's thermo-diffusion apparatus[25,36] to produce ^{33}S at high concentration.

In addition to the hydrogen sulphite process, the exchange of isotopes between potassium xanthate $S{=}C(OR)(SK)$ and carbon disulphide CS_2 has also been studied as a means of separating sulphur and carbon isotopes simultaneously[104,105]. The lower flow reversal in this process uses the reaction

$$RO{-}C(SK){=}S + HCl \rightarrow ROH + KCl + CS_2$$

and the upper flow reversal uses the reaction

$$CS_2 + KOH + ROH \rightarrow RO{-}C(SK){=}S + H_2O\ .$$

This process is not very attractive for the separation of sulphur isotopes, because sulphur isotope exchange is very slow in the C–S and O–S bonds[20]. Furthermore, the practical value of the method is very doubtful in view of its reliance on expensive chemical flow reversal arrangements.

Table 7. Separation of sulphur isotopes in chemical isotope exchange processes between SO_2 and its thermally unstable complexes (p = 0.1 MPa).

Working system	ε	10^4G, $m^3\ m^{-2}\ s^{-1}$	T, K	K^∞ (γ^∞)	Refs.
$^{32}SO_2$–[pyridine/H_2O] × $^{34}SO_2$* (43% pyridine)	5.5 M	4.72	357	(4.55% ^{34}S)	[94]
ditto	4.5 M	4.72	323	(1.15% ^{34}S; 1.075% ^{33}S)	[94]
$^{32}SO_2$–[pyridine/H_2O].$^{34}SO_2$ (4.7 mole C_5H_5N litre^{-1})	4.5 M	4.72	323	1.15	[95]
$^{32}SO_2$–[pyridine/H_2O/H_3PO_4] × $^{34}SO_2$ (3.15 mole H_3PO_4 litre^{-1}, 2.86 mole C_5H_5N litre^{-1})	1.95 M	1.88÷2.2	295	1.13	[95]
$^{32}SO_2$–[pyridine/H_2O/H_3PO_4] × $^{34}SO_2$ (3.33 mole H_3PO_4 litre^{-1}, 2.77 mole C_5H_5N litre^{-1})	1.5 M	2.05	294	1.135	[95]
$^{32}SO_2$–[pyridine/H_2O/H_3PO_4] × $^{34}SO_2$ (4.39 mole H_3PO_4 litre^{-1}, 2.89 mole C_5H_5N litre^{-1})	1.56 M	1.732	293	1.08	[95]
$^{32}SO_2$–H_2O.$^{34}SO_2$	0.9 M	2.83÷3.46	293	1.075	[95]

*H_K = 1.85 m, D_K = 25 mm, triangular spirals of V2A steel wire, 1.6 × 1.6 × 0.2 mm.
**H_K = 2.0 m, D_K = 25 mm.

Symbols: as in Table 6.

2. Systems Using Thermal Flow Reversal

The possibility of using complexes of SO_2 with various organic compounds has been studied in several laboratories (see Tables 4 and 7). The systems examined include xylidene and dimethylaniline[55,81,82,87], pyridine[55] and its mixtures with water and phosphoric acid[94,95], and also diethyl and dimethyl ether, anisole, and phenetole[75,84,106], trimethoxyborane and acetonitrile[83], and aniline, triethylaniline, ethylene oxide, phenol, and tetrahydropyran[55]. Other sulphur-containing complexes have also been studied, including those formed by the reaction of H_2S, $(CH_3)_2S$, CS_2, COS, $SOCl_2$, SCl_2, and S_2Cl_2 with complexing agents such as diborane, boran trifluoride, boron triaryls and trialkyls, and also aluminium trialkyls (in particular, $(CH_3)_3Al$ and $(C_2H_5)_3Al$).[107] The largest isotope effect was obtained for a mixture of SO_2 and the complex of SO_2 with the pyridine–water azeotropic mixture: on a column 1.85 m long this gave a separation of the ^{32}S and ^{34}S isotopes of $K^\infty = 1.15$.[95]

Though these systems offer the great advantage of thermal flow reversal, they are not serious competitors of the hydrogen sulphite system for the separation of sulphur isotopes. In most cases their α values are extremely low (see Table 4), and the low stability of the complexing agent towards atmospheric oxygen and water vapour can create serious practical problems. As a result, the separation has to be carried out in an inert atmosphere, and provisions for continuous (or periodic) drying have to be made, together with provisions for removing the decomposition products of the complexing agent. We should also note that the complexing agents and the sulphur-containing compounds listed above are, in most cases, highly toxic and corrosive.

However, these difficulties should not be used as an argument to stop the research in these areas, because analogous systems have long been used with success in industrial plant for the separation of boron isotopes[108].

The most important outcome of these investigations is the establishment of clear correlations between the parameter α and the physicochemical of structural properties of the complexes. However, before examining these correlations we should briefly consider the reliability of the α values listed in Table 4 for the SO_2 complexes. These values were obtained either by repeated equilibration or by separating a mixture of isotopes on a column. The weakness of the latter method has already been stressed in this review. The main weakness of the repeated equilibration method is its reliance on a strict preservation of the material balance[109–112], which cannot always be ensured owing to mechanical losses or to the volatility of the gaseous sulphur compounds. The results may be distorted also by kinetic isotope effects in the evolution of the gaseous sulphur compound from the complex former (or its absorption). Furthermore, errors in the determination of α may arise from fluctuations (from step to step) in the amount of flow contraction assumed for the calculation[109,110,117].

These factors may be responsible for the large discrepancies in the α value for the SO_2–SO_2·dimethylaniline system (see Table 4) and for the good agreement of the α values in the SO_2–SO_2·xylidene system for the ^{34}S–^{32}S and ^{33}S–^{32}S isotope mixtures. Another possible reason for the poor reproducibility of experimental data is the dependence of the separation coefficient α on the composition of the complex (or, more exactly, on the parameter r, which is the ratio of the number of moles of the sulphur-containing compound in the complex, D, to the number of moles of complexing agent, R). This dependence is due to the presence in the liquid phase of free molecules of the sulphur-containing compound, leading to inter-phase isotope exchange (in addition to ordinary isotope exchange) between the sulphur compound in the gas phase and in the liquid complex former respectively. Therefore the observed effective separation coefficient α depends on the fractional amount m of free sulphur compound in the liquid phase according to the equation

$$\alpha = mK_{ph} + (1-m)K$$

where K is the equilibrium constant of the isotope exchange reaction between the sulphur compound in the gas phase and its complex in the liquid phase, and K_{ph} is the separation

coefficient for the inter-phase isotope exchange between the free sulphur compound in the gas phase and in the liquid phase respectively.

A rational search for efficient working systems by quantum-statistical calculations can be based on the ratio of the partition functions (β-factors) of the isotopic forms of the sulphur compounds[61,113]. In addition to an estimate of the equilibrium constants for different sulphur compounds this calculation gives an indication of the trends in the dependence of the β-factor on various characteristics of the compounds, as in the earlier work on boron compounds[113–116]. However, the calculation assumes that the vibration frequencies and the anharmonicity factors for both the normal and the isotopic molecules are experimentally known, and in the case of the more complex molecules these measurements are extremely difficult[115]. Reported calculations[61,85] suggest that the SO_3 and SO_2 molecules should have the highest β-factor of all gaseous sulphur compounds. At the same time these calculations point to the advantages of using a thermally unstable complex (e.g. a complex of H_2S) for the separation of sulphur isotopes.

A relationship has been reported[118,119] between the parameter α for sulphur isotopes and the ionisation potential J of the complexing agent. These calculations were based on the wave function

$$\varphi_N = a\varphi_0(RD) + b\varphi_1(R^+ + D^-)$$

which describes the ground state of the complex molecules ($R + D \rightleftharpoons RD \rightleftharpoons R^+ + D^+$), and assumed a linear dependence of the separation coefficient α on the ionisation potential J of the donor: $\alpha = m - nJ$, where m and n are constant coefficients, equal to 1.0109 and 9.8×10^{-4} respectively for the separation of the sulphur isotopes ^{32}S and ^{34}S in SO_2–SO_2(complex) systems at 293 K.

The above equation is not acceptably consistent with experiment[118], and it assumes that the isotope effect is negligible for $J = 11.1$ eV. Since the potential J usually decreases as the size of the molecule increases, we can expect[118] α to increase with the molecular weight of the donor. As Table 4 shows, this expectation is not borne out in general: for different homologous series the parameter α tends to increase with the molecular weight of the complexing agent, but within any one homologous series no such tendency is observed.

It has also been pointed out[118] that the choice of a linear correlation between α and J is purely empirical, and there may be exceptions arising from steric hindrance to the formation of additive compounds, from orientation effects, or from the screening effect of free electrons. Furthermore, the assumed correlation between the ionisation potential and the properties of the resulting donor–acceptor complex has been shown[120] to be valid only if the complex forming power and the ionisation potential are referred to the same system of electrons in the donor molecule. In aliphatic or in saturated cyclic ethers, sulphides, or amines both these quantities refer to the properties of the unshared pair of electrons on the hetero-atom, but in aromatic or unsaturated compounds containing a hetero-atom the ionisation potential may relate to the excitation of a π-electron whereas the formation of the complex takes place through an n-electron of the hetero-atom. Furthermore, the use of the ionisation potential of the donor molecule to characterise the donor–acceptor interaction fails to take account of the overlap of the orbitals involved in the formation of the intermolecular bond and of "spatial" factors.

It has therefore been suggested[120] that the donor–acceptor interaction (and therefore also the parameter α) could be more accurately characterised by using the overlap integrals of the atomic orbitals of the donor and the acceptor. The possibility was demonstrated[120] for the complexes of BF_3 with a class of amines, ethers, and thio-ethers in which α varies in the order $\alpha_S > \alpha_O > \alpha_N$ whereas the overlap integrals calculated by using the Slater functions for the B–O, B–N, and B–S bonds vary in the opposite order (B–S < B–O < B–N). It is interesting to note that in these classes of compounds the ionisation potential decreases in the sequence $J_O > J_S > J_N$.[121] This tends to support the correlation proposed in Ref.118.

A dependence of α (or of the equilibrium constant K of the isotope exchange reaction) for a series of compounds of a given type has been noted[108] as a function of the nature of the electron-donor atom in the complex former R, of the nature and position of the complex former in the homologous series, of the presence of polar or easily polarisable groups in the molecule, and of the structure of R. The effects were ascribed to the factors listed above and their influence on the stability of the complexes, and in particular to the heat of formation of the complex ΔH_{form}. The relationship between α and the heat of formation of the complex was specially stressed[108]. In the case of boron complexes of a single type the parameter α was found to increase as the stability of the complex decreases, i.e. as ΔH_{form} decreases. In such a series of complexes the stability decreases as the atomic number of the donor atom increases, due not only to the larger size of the atom but also to the screening of the inner electrons from the electrons in the outer sphere of the donor atom. These considerations led to the suggestion[107] that the α values for a series of sulphur complexes of a given type including B, Al, Ga, In, or Tl as the electron-donor atom should decrease in the sequence Tl > In > Ga > Al > B. At the same time, the data on the boron complexes indicate that in the case of sulphur complexes the α values should decrease in the sequence Se > S > O > N.

Clearly, in the sulphur complexes (as in the BF_3 complexes) the maximum value of α is found in the second member of the homologous series of complex formers. This was confirmed experimentally[55,75] in a study of the separation of sulphur isotopes by using the complexes of SO_2 with phenol[55] and with anisole and phenetole[75]. Whereas by using phenol no separation was obtained in a column 0.84 m long, by using anisole in a column 1 m long with a packing of particle size ($1.6 \times 2.0 \times 0.2$) $\times 10^{-3}$ m a stationary distribution of ^{32}S and ^{32}S corresponding to a separation of $K^{\infty} = 1.06$ was obtained, and this was greater than the separation obtained in the same column by using phenetole. The maximum in the α values for the second member of the homologous series of complex formers has been ascribed[108], in the case of the separation of boron isotopes, to the influence of the geometry of the R molecule on the energy of the bond between the donor atom and the boron atom, and hence on the parameter α. This explanation can be extended to the complexes formed by sulphur-containing compounds, since the influence of the structure of the complex former on α is unmistakable in the results (Table 4) for the complexes of SO_2 with aniline ($\alpha = 1.002$)[55] and with dimethylaniline ($\alpha = 1.013$)[81]. The presence of two methyl groups on the donor (nitrogen) atom of dimethylaniline causes steric hindrance to the formation of a donor–acceptor bond between the sulphur and the nitrogen atom, thus lowering the stability of the complex and as a result raising α.

In the case of the BF_3 complexes the introduction of polar or easily polarisable groups into the complex-forming molecule lowers the stability of the complex: conversely, the stability is increased by the introduction of electron-donor substituents[108]. Thus the parameter α can be varied by inserting appropriate groups into the complex-forming molecule. However, we should not that the tendency of α to

increase in response to a decrease in the stability of the complex (by the introduction of polar or easily polarisable groups) also leads to a decrease in r. We also note that because of the scarcity and unreliability of the published data on the heat of formation of the complexes of sulphur-containing compounds it may be necessary to use the composition r (at saturation) as a measure of the stability of these complexes.

Table 8. Vapour pressure of the complex (p) against composition (258 K, SO_2 partial pressure 0.1 MPa).[106]

SO_2:$(C_2H_5)_2O$ *	p, MPa	SO_2:$(C_2H_5)_2O$ *	p, MPa
1.000	0.01167	0.334	0.0526
0.845	0.01395	0.227	0.0625
0.570	0.0295	0.111	0.0721
0.510	0.0334	0.000	0.0796

*Molar ratio.

Some data on the phase equilibria in systems including sulphur complexes are given in Table 4. The properties of complexes of the $(CH_3)_2O\cdot SO_2$ and $(C_2H_5)_2O\cdot SO_2$ type have also been studied[84,106]: for $(C_2H_5)_2O\cdot SO_2$ the dependence of the vapour pressure p on the composition r was determined for 258 K and a partial pressure of SO_2 of 0.1 MPa (see Table 8), whereas for $(CH_3)_2O\cdot SO_2$ an azeotrope containing 58% SO_2 and 42% $(CH_3)_2O$ was observed at 273 K. The degree of dissociation of the latter complex in the vapour phase at 273 K was found to be 0.93. The melting point and boiling point of the $(CH_3)_2O\cdot SO_2$ complex are given[84] as 177.5 and 263 K respectively, and its heat of formation as ~15.5 kJ mole^{-1} (the composition of the saturated complex r = 1 mole SO_2 mole^{-1} $(CH_3)_2O$ is reached at 263 K and 0.1 MPa). The boiling point of $(C_2H_5)_2O\cdot SO_2$ is given[106] as 258 K, and its heat of formation as ~29.4 kJ mole^{-1}.

Attempts to relate the separation coefficient to the polarisability and dipole moment of the complex former have been described[122,124]. The more readily polarisable the complex former, and the larger the dipole moment of the complex, the weaker is the bond formed in the complex. Therefore we can expect α to increase with the dipole moment of the complex. This expectation has been confirmed experimentally for the complexes of BF_3 with the lower olefins, and is probably equally valid for the complexes of sulphur-containing systems. The dipole moments of some selenium, sulphur, and phosphorus compounds and their complexes are listed in Ref.125.

The importance of establishing the correlation between α and the parameters which describe the electronic and structural properties of the donor molecules and their substituents has been stressed[126,127]. By classifying the effect of substituents on the properties of the donor molecule as inductive, steric, mesomeric, etc. we can write the following expression for α in terms of the Hammett–Taft equation

$$\lg \alpha/\alpha_0 = \rho\Sigma\sigma + \Delta n \cdot h + \delta E_S + \psi$$

where α_0 and α are the separation coefficients of the sulphur isotopes for the initial and the substituted compound respectively, σ is the inductive constant (a measure of the effective electronegativity of the substituents), E_S is the steric constant of the substituent, Δn is the difference in the numbers of hydrogen atoms involved in hyperconjugation in the initial and the substituted compound, ρ, δ, and h are the parameters of the reaction series (a measure of the sensitivity of the reaction to the inductive, steric, and hyperconjugation effects respectively), and ψ is the coefficient which reflects the contribution from the conjugation of any π system to the reaction centre. Values of σ, E_S, and Δn are available for almost any substituent[128]. Often some of the effects can be ignored, and the equation becomes simpler.

In conclusion we note that all the complexes of SO_2 and of other sulphur compounds can be arbitrarily divided into two large groups. The first group includes complexes whose vapour pressure is lower than that of the complex former (for example, $(CH_3)_2O\cdot SO_2$ and $(C_2H_5)_2O\cdot SO_2$). These are only partially dissociated in the vapour phase, and as a result the gaseous sulphur compound included in the complex cannot be separated from the complex former. This group of compounds can be used in the separation of sulphur isotopes by chemical isotope exchange combined with distillation, involving isotope exchange between the liquid and the partially dissociated vapour of the complex. The lower flow reversal is achieved by evaporation of the liquid complex.

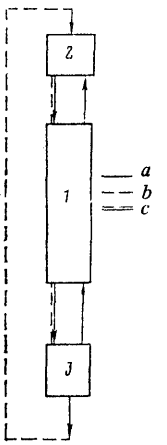


Figure 4. Process for the separation of sulphur isotopes by chemical isotope exchange with thermal phase reversal: *1*) exchange column, *2*) adsorber, *3*) desorber; *a*) gas flow, *b*) flow of complex former, *c*) flow of complex.

The second group of complexes includes those whose vapour pressure is greater than that of the complex former (for example, $C_6H_5OCH_3\cdot SO_2$, $C_6H_5OC_2H_5\cdot SO_2$). These complexes are almost fully dissociated in the vapour phase. By heating them to the boiling point of the complex former it is possible to strip the sulphur-containing gas almost quantitatively from the complex, since the vapour pressure of the complex former is relatively low. This makes possible the separation of sulphur isotopes by counter-current exchange between a gaseous sulphur-containing compound and its liquid complex, i.e. by "clean" chemical isotope exchange (Fig.4). Flow reversal at the ends of the separation cascade is achieved by thermally dissociating the complex in the desorber to the sulphur-containing gas and the complex former. The complex former is cooled and re-used to absorb the gas emerging from the separating column in the upper flow reversal unit, which is also an apparatus of the column type[108].

We should stress that the possibility of exploiting this group of compounds for separating sulphur isotopes was first demonstrated by Soviet workers[81]. Evidently, solid complexes of sulphur-containing gases could also be used, as in the gas–solid hypersorption processes proposed for the separation of hydrogen, nitrogen, and oxygen isotopes[129–131]. High values of r and α can be expected with these complexes. Furthermore, solid complexes of gaseous sulphur compounds can be used in separation processes as liquid solutions in solvents inert towards both the compounds and their complexes. However, the use of a solvent may have an unfavourable effect on the economics of the process because of the energy cost of heating, cooling, and transporting the solvent, and also because of the decreased throughput of the column. Nevertheless the use of a solvent could improve the rate of isotope exchange in the columns.

Table 9. Sulphur isotopic equilibrium data for ion exchange systems at 298 K.

R	α	Method	References
	$H_2{}^{34}SO_3$–$RH^{32}SO_3$		
Wofatit L	1.0064	3,13	[101]
SBW	1.0064	3	[101]
SBR	1.0064	3	[101]
	$^{34}SO_2$–$RH^{32}SO_3$		
Wofatit L	1.010	13	[101]
SBW	1.010	13	[101]
SBR	1.010	13	[101]
	$NH_4H^{34}SO_3$–$RH^{32}SO_3$		
Dowex 2-x 8.5-100 mesh	1.010	13	[17]

Symbols: methods of determining α: *13*) chromatographic; other symbols as in Table 1.

Table 10. Separation of sulphur isotopes by ion exchange* (T = 293 K, P = 0.1 MPa).[101]

c, mol litre^{-1}	v, m s^{-1}	HETP, cm	K_τ
0.5	15.5	6.0	1.13
1.0	15.5	10.0	1.10
1.0	15.5	7.0	1.15
0.4	1.332	1.3	1.42
0.4	4.0	2.1	1.36
0.4	8.5	4.5	1.21
0.4	14.33	4.6	1.20
1.0	0.833	1.1	1.59
1.0	8.5	1.9	1.44
0.125	8.33	5.3	1.19
0.6	4.17	2.6	1.11
0.4	4.0	2.8	1.35
0.4	4.34	3.8	1.38
0.4	4.17	5.6	1.24
0.4	4.17	11.7	1.32
1.0	5.0	2.8	1.38
0.4	4.17	4.6	1.64
—	—	0.2	23% ^{34}S **

Symbols: c is the concentration of the solution, v is the velocity of the liquid phase, K_τ is the degree of separation achieved.

*Separation carried out in the $RH^{32}SO_3$–$NH_4H^{34}SO_3$ system, where R is Dowex 2-X (8.5)-100 mesh, H_K = 12 m, D_K = 25 mm.

**Data from Ref.117; the maximum concentration of ^{34}S reached is stated. The same system was used, with H_K = 0.85 m and D_K = 47 mm.

IV. ION EXCHANGE PROCESSES

Extensive work carried out during the 1960's in Sweden[17], East Germany[83,101,132,133], and France[60] demonstrated the possibility in principle of using ion exchange processes in the separation of sulphur isotopes (see Tables 9 and 10), and resulted in the production of gramme quantities of the isotopes[17]. Separation in columns was achieved by using Spedding's method[134] of organising a counter-current process on ion exchangers without motion of the solid phase. However, the low HETP values thus obtained are insufficient compensation for the disadvantages of ion-exchange separation, including the high consumption of reagents for flow reversal and regeneration of the resin (thus, the production of 1 mole of ^{33}S in the NH_4HSO_3–Dowex resin system requires[17] the expenditure of 4×10^4 mole of HCl and $\sim 5 \times 10^4$ mole of NH_4HSO_4), and also the complexity of the apparatus, due to the difficulty of arranging a continuous counter-current process in this type of system[135–137]. Similar problems are encountered in processes using liquid anion exchangers. Isotopic mixtures of ^{32}S and ^{34}S have been separated in an experimental column at 298 K by using the following working systems: CCl_4/tri-n-octylamine $H{\cdot}HSO_3/H_2SO_3$, C_6H_6/tri-n-octylamine $H{\cdot}HSO_3/H_2SO_3$, n-octanol/tri-n-octylamine $H{\cdot}HSO_3/H_2SO_3$, toluene/tri-n-octylamine $H{\cdot}HSO_3/H_2SO_3$, cyclohexane/tri-n-octylamine $H{\cdot}HSO_3/H_2SO_3$, tetralin/tri-n-octylamine $H{\cdot}HSO_3/H_2SO_3$, nitrobenzene/tri-n-octylamine $H{\cdot}HSO_3/H_2SO_3$, pentane/tri-n-octylamine $H{\cdot}HSO_3/H_2SO_3$, and hexane/tri-n-octylamine $H{\cdot}HSO_3/H_2SO_3$. Separation was observed in every case, but the α and HETP values were not determined[83]. In spite of the almost two-fold saving in materials achieved by combining the ion-exchange separation of sulphur isotopes with the separation of carbon isotopes[83, 132,133], the disadvantages of the method still make it unacceptable in practice. A possible combined scheme, relying on the use of acids of different strength for the separation, is shown in Fig.5.

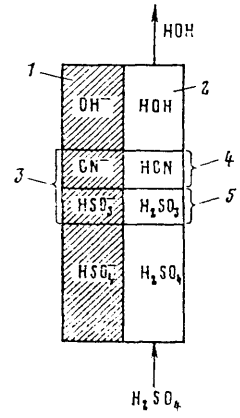


Figure 5. Combined ion-exchange separation process for sulphur and carbon isotopes: *1*) solid phase, *2*) liquid phase, *3*) separation part of the column, *4*) carbon isotope separation zone, *5*) sulphur isotope separation zone.

A far more promising method is based on continuous counter-current adsorption processes, analogous to those previously used to separate nitrogen or oxygen isotopes[130,138],

since these offer α values usually much greater than those obtained in ion exchange or in distillation as well as the possibility of thermal flow reversal.

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Thus we may conclude that studies of equilibrium two-phase counter-current processes for the separation of sulphur isotopes have not yet led to the development of a really efficient process, combining low cost with other desirable attributes, in spite of the pressing need for such a process in both scientific and industrial practice. The most promising directions for future development work include: a search for new and more effective working systems, optimisation of the technological parameters of the separation processes, the development of rational technological schemes for combining the separation of sulphur isotopes with other chemical or isotopic production processes, and a search for means of using cheaper energy sources for phase reversal, and for means of utilising the waste products.

The main aim of the work should be to establish relationships between the physicochemical properties of the working systems and their separation coefficients, rate of isotope exchange, and other characteristics of the separation process.

From the industrial point of view it would be desirable to investigate new systems compatible with thermal flow reversal. The most promising of these are the various adsorption processes, and also the chemical isotope exchange between SO_2 and its thermally unstable complexes in the solid form, or dissolved in an inert solvent.

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Prediction and Analysis of Heterogeneous Catalysis Mechanisms by Pattern Recognition Methods with a Computer

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The basic aspects of the prediction of catalytic activity in one-component and multi-component heterogeneous catalysts and of the analysis of the mechanism of heterogeneous catalytic reactions by using pattern recognition theory with a computer are discussed. The present state of development is reviewed, and examples of the use of this method in choosing catalysts for different types of reaction are given. 53 references.

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I. INTRODUCTION

Catalyst prediction should be clearly distinguished from the search for entirely new types of catalyst, or for catalysts for new and unexplored classes of reactions†. Catalyst prediction denotes the *a priori* search for suitable catalysts for known types of reaction on the basis of existing information on a range of potential catalysts and of a general understanding of the mechanism of their action. As well as having the right chemical composition, an effective industrial catalyst should have the required permeability (or porosity) parameters, including strength and geometric size. In this review we shall be concerned exclusively with the problem of predicting the chemical composition of the catalyst, though the pattern recognition algorithms are equally applicable to the prediction of the physical parameters of the catalysts.

By using the existing level of scientific understanding of catalytic reactions, and the vast fund of empirical information (extending over more than a century), we can often select suitable catalysts for various reactions, including new reactions, if they fall within one of the main classes of chemical transformation (e.g. hydrogenation, oxidation, condensation, etc.). However, this type of prediction offers no information on the productivity or selectivity of the catalyst, parameters of the utmost importance in industrial applications. We should note that in large-scale industrial production even a small improvement in performance could be very important economically.

Modern ideas on catalysis, such as the relationship between catalytic action and the acid–base properties of the surface[1,2], the energetics of the interatomic bonds of the lattice[3,4], the stabilisation energy of the crystal field[5], the geometric parameters of the lattice, etc. can be used to construct an acceptably rational scheme for the selection of catalysts for stated reactions[6–8]. However, in spite of its attractiveness and of its usefulness in research this scheme cannot predict quantitatively the main practical characteristics (activity, selectivity, etc.) of the proposed catalysts.

† Throughout this review the term catalyst will be used to denote heterogeneous catalysts.

In the present state of knowledge we can distinguish three possible paths for catalyst prediction: 1) the theoretical approach, based on the theory of the structure of chemical compounds and on quantum chemistry, 2) the semi-empirical approach, based on correlation methods, and 3) the mathematical (heuristic) approach, which relies on the methods and algorithms of the mathematical pattern recognition theory.

In spite of the important advances recently made in the quantum chemistry of heterogeneous catalysis[9–11] the first approach is still far from the state of development which would justify quantitative predictions of the output parameters of the catalysts. Nevertheless, as we shall show below, theoretical (and especially quantum-chemical) considerations play an important role in computer methods of catalyst prediction.

The second approach is equivalent, in practice, to using one of the many variants of the principle of linear free energy relationships (LFER), such as Balandin's principle of energy correspondence, or the Brønsted, Hammett–Taft, or Voevodskii–Semenov equation. Numerical calculations by these equations are possible only for empirical coefficients, and are only valid for catalysts of a single type used in one particular reaction of (in the case of a group of homologues) for one catalyst in one reaction. These methods are unsuitable for predicting multi-component catalysts and they do not reveal extrema in the quantities being correlated (except the Balandin method, which is not accurate enough, however). Nevertheless investigations in this direction are continuing. Empirical correlation equations have been obtained for the hydrogenolysis of ethane and of alcohols[12,13] and for the dehydrochlorination of chloro-ethanes on sulphates[14]. These problems are discussed in depth in Ref.9.

Unlike the LFER methods, the pattern recognition methods do not need to be confined to catalyst (or reaction) analogues: though the mathematical recognition methods when applied to structure–property problems are effectively methods of detecting multi-dimensional or multi-level correlations they differ from the classical correlation analysis methods in their ability to reveal the inter-relationship of ten or more properties used as indicators of the quality of the samples by taking the combination of criteria into account. This feature of the pattern recognition methods has already led

to their successful application in chemical problems such as the determination of molecular structure from spectral data, the *a priori* calculation of the properties of inorganic compounds, and the prediction of biological activity in organic compounds[15–17].

The most important aspect of the pattern recognition methods as applied to catalysis problems is their ability to exploit the very large fund of experimental information on catalysts in standard handbooks[18] or in original publications as a predictive basis. The published data differ widely in precision and reliability: they include misleading information introduced for patent reasons, and they are only valid in statistical, computer-aided information processing methods such as the pattern recognition methods.

The use of these methods for the prediction of catalyst behaviour is made easier by the level of reliability required, which can be very high in some applications but not in catalyst prediction. Thus in radar, medicine, and geological prospecting the probability of the prediction must be 99.5% or more. In the case of catalyst selection an economically effective forecast is achieved simply by short-circuiting a laborious empirical search, and increasing the probability of finding the optimum catalyst. Since in any case the prognosis must be tested experimentally, there is no danger of making a "catastrophic" mistake. As compared to catalyst selection by the conventional semi-empirical methods, a quantitative prediction with a probability of ~80–85% would be economically effective.

The potential value of pattern recognition methods in the search for optimum catalysts is confirmed by calculations of their effectiveness[19,20]. In recent years pattern recognition methods and related methods of mathematical statistics have been used by many workers. Thus in Refs. 21–24, discussed below in detail, pattern recognition algorithms are used to identify catalysts for the hydrogenation and synthesis of thiophen. The factor analysis method has been used[25,26] to predict catalysts for electrochemical processes. Some results obtained by the present writers since the publication of their monograph[9] and only partially reported[27–29] will also be discussed in this review.

Essentially all recognition methods consist in establishing step-by-step relationships between the parameters of the solid responsible for its catalytic properties and its other physicochemical properties. These parameters include (depending on technological and cost considerations) either the productivity of the catalyst in terms of the desired product (i.e. its activity) or the selectivity of the reaction (or process) when catalysed by this material. The latter quantity is defined as the yield of desired product expressed as a percentage of the theoretically possible yield (or of the potential yield in petroleum chemistry), and it corresponds to the selectivity of the anion of the catalyst itself. In special cases other selection criteria are possible; for example, the operational life of the catalyst, its thermal stability, etc.

Since the recognition algorithms allow the ranking of the properties with respect to their effect on the useful parameters of the catalyst we can also solve the inverse recognition problem, i.e. identify the most "influential" physicochemical properties of the catalysts and reactants from the point of view of ensuring a fast and selective reaction. The results obtained give a basis for proposing the mechanism of the catalytic action. The main value of this method of analysing the mechanism of catalysis lies (as in the case of catalyst prediction) in the ability to exploit the extensive but not always very accurate experimental information, and to obtain reliable results by virtue of the statistical treatment implicit in the pattern recognition algorithms.

II. FUNDAMENTALS OF PATTERN RECOGNITION METHODS

Pattern recognition theory is a branch of cybernetics. The mathematical foundations of the methods used in pattern recognition are fully discussed in textbooks[30–32]. In this Section we shall merely give a short description of the methods which have been used in chemistry to predict the properties of substances.

The solution of the recognition problem is based on empirical input data, called the "training sample". In our case the "training" consists in "tuning" the specially developed algorithms in a way which enables the computer to determine the property of interest to the experimenter from the structure of the materials. The term structure denotes the set of primary properties of the material which can be used as criteria. The training process includes separating the materials into classes according to the value of the property being predicted. The assignment to one of these classes of a material not included in the training sample is the solution of the pattern recognition problem.

Existing recognition algorithms are either "deterministic" or "statistical". The former include the algorithms based on geometric considerations, and the perceptron algorithms, developed as a model of the perception of patterns by human beings[33]. The latter class includes the algorithms of the stochastic approximation and those based on the principles of statistical decision making. A special group, only recently recognised, consists of algorithms which have been called syntactic[34]. So far only algorithms from the deterministic group have been used in chemical problems. The desirability of using other types of algorithm to solve these problems will be considered below.

Let us examine more closely the geometrical treatment of the recognition problem. In this treatment the set of criteria of the objects to be recognised is treated as a hyper-space with one coordinate axis for each criterion. In such a space each object is represented by a point whose coordinates give the numerical values of the criteria. Coordinates corresponding to qualitative criteria can also be used: this is done by numbering the possible realisations of the qualitative criterion and equating the numbers to the values of the coordinate on the axis for that criterion. Since the limits and the ranges of the characteristics used as criteria are always known it is convenient to adopt a system of dimensionless units such that all possible objects lie within a unit cube of the criterion space.

In property forecasting it is a natural assumption (and one consistent with our chemical intuition) that substances whose Euclidean distance apart in the criterion space is small will have similar properties. This hypothesis underlies the application to the chemical problem of algorithms based on geometrical considerations. The geometric treatment includes algorithms which have been used successfully in catalyst prediction problems (potential functions, and binary or segmented linear classifiers).

The simplest of these algorithms is the binary linear classifier. Its action consists in finding a hyper-plane which divides the objects into two classes: the "dichotomy" problems. It is convenient to make this plane pass through the origin of the coordinate system. This can be done by introducing an additional $(N + 1)$-th coordinate (where N is the number of criteria of interest) whose value is assumed to be the same for all the objects (Fig. 1). In this space any dividing plane is uniquely defined by the unit vector of the normal **W**, called the weight vector. The vector **W** is found by an iterative process, during which the positions of the objects in the training sample relative to an arbitrarily chosen initial plane are tested sequentially. If an object

(radius vector $\mathbf{R}_k$) is found to be incorrectly classified, the position of the plane is correlated accordingly, and its new vector is expressed as the linear combination

$$\mathbf{W}' = c_1\mathbf{W} + c_2\mathbf{R}_k$$

The coefficients c_1 and c_2 are determined from the normalising condition of the weight vector and from the expression

$$\mathbf{W}' \cdot \mathbf{R}_k = -\mathbf{W} \cdot \mathbf{R}_k$$

If this condition is satisfied the kth object is on the correct side of the new plane and at the same distance from it as from the initial plane. It can be shown[35] that if a dividing plane exists, i.e. if the classes are linearly separable, this iterative process always converges.

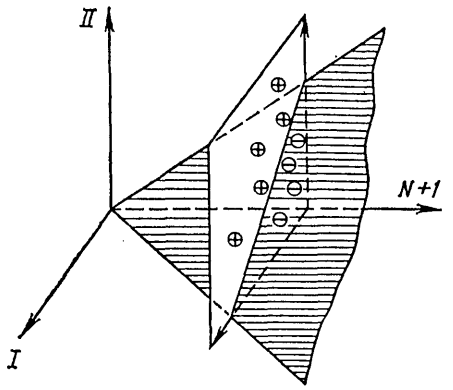


Figure 1. Dividing plane in criterion space, with an additional coordinate.

Unfortunately, linear separability into classes is seldom found. The boundaries of the classes usually have a more complex structure, and a simple linear classifier is inadequate. This weakness of the algorithm can be partly overcome by replacing the dividing plane by a plate of finite thickness and treating the objects lying within its thickness as unclassifiable. The thickness of the dividing plate is called the threshold, and the algorithm is called a linear classifier with non-zero threshold[15].

Even more flexible is the segmented linear classifier: a generalised form of the linear classifier in which the dividing surface is formed by a set of planes. In this algorithm a correction is applied to the position of the planes when the object is incorrectly classified with respect to the majority of the planes[35].

Linear classifiers have been widely used, and in spite of their simplicity they have been found to be effective in a wide range of recognition problems (including chemical ones)[15]. Many more complex binary classifiers, in which the dividing surfaces are not linear, can be reduced[35] to algorithms of this type. With any of the above algorithms the objects can be classified into three or more groups by sequential dichotomies, i.e. by repeating their application to the already classified populations.

Another geometric approach used in pattern recognition theory is the potential functions method, which relies on the concept of a potential for the kth object in the criterion space, $u(|\mathbf{R}-\mathbf{R}_k|)$, and a potential for the α class of objects,

$$U_\alpha(\mathbf{R}) = \frac{1}{N_\alpha} \sum_{k \equiv \alpha} u(|\mathbf{R} - \mathbf{R}_k|)$$

where N_α is the number of objects in the class. The boundary between the two classes (α and β) is taken to be the surface on which the potentials are equal:

$$U_\alpha(\mathbf{R}) = U_\beta(\mathbf{R})$$

It is convenient to choose for $u(x)$ a continuous, monotonically decreasing function having a finitie value at $x = 0$, for example

$$u(R) = 1\ (a + bR^2),\ a > 0$$

As in the case of binary classifiers, in the potential functions method objects are most easily classified into a large number of groups by successive dichotomies. At each step the assignment to one of two classes is determined by the sign of the difference between the potentials, $U_\alpha - U_\beta$. A more detailed discussion of the application of the potential functions algorithm can be found in textbooks[9,36].

Without attempting to examine in depth the principles of the perceptron theory (see, for example, Refs.30 and 33) we can define the method as the classification of a set of objects in terms of the sets of values of the criteria prescribed for each class. In catalysts prediction and similar problems the algorithms and programs based on logic functions[37] are more useful than the classical perceptron. The advantage of this approach lies in the possibility of defining classes forming an interpenetrating system of the "water in a sponge" type. The principle has been used for catalyst prediction in the "Prognoz-73" program[9], which relies on the following algorithm. Ranges of values are defined for all the properties of the catalysts. The number of criteria is assumed to be equal to the total number of ranges, and each criterion can take the values 1 or 0 depending on whether the property lies within or outside the range. Thus each catalyst is associated with a Boolean (logic) vector. We can now construct the discriminant conjunctions, i.e. the Boolean vectors whose termwise logic product with any vector from the class of effective catalysts is equal to the same vector and whose product with the vectors from any other class is equal to the zero vector. By using the discriminant conjunctions any catalyst can be assigned to one of the classes.

The recognition algorithms described in this Section are far from exhausting the enormous range of possible approaches to the solution of problems in this rapidly expanding field of applied mathematics. They do, however, give a clear illustration of one of the most important ways of "recognising": the assignement of an unknown object to a defined class. This includes preliminary training (in other words, tuning) of the algorithm by using an existing sample of already classified objects. As a rule, recognition algorithms are not "ideally" tunable. We must therefore introduce a new concept: the classifying power α_{cl} of the algorithm, defined as the ratio of the number of correctly classified objects to the total number of objects in the training sample#. The next step is to apply the trained algorithm to the unknown objects. The ratio of the number of objects which subsequent experience shows to have been correctly classified to the total number of objects investigated is called the predictive power of the algorithm α_{pr}.

The parameter α_{cl} is determined by carrying out a prediction for each object in the training sample with the recognition algorithm trained by using the remaining (N − 1) objects.

The coefficients α_{cl} and α_{pr} calculated in this way should be treated as arbitrary quantities, depending on the size and composition of the sample. Adequate estimates of the true classifying power and predictive power are obtained if sufficiently representative (or generally valid) samples are used. An important characteristic of the general validity of the sample is the ratio of its volume to the number of criteria used in the recognition, denoted by the symbol λ. It is usually assumed that successful prediction requires a fairly large value of the ratio λ, which we shall term the relative sample volume ($\lambda > 2$, say). However, there is evidence that satisfactory solutions of applied problems can be obtained also with much smaller values of λ.[38]

We should stress that problems requiring detailed statistical analysis of the pattern recognition results are only seldom included in current publications, and will not be considered in this review.

III. PREDICTION OF ONE-COMPONENT CATALYSTS OR PROMOTERS

The problem most simply solved by pattern recognition theory is the prediction of one-component catalysts. In this case the choice of a new catalyst (metal, oxide, etc.) can be made by comparing existing experimental data on the activity and selectivity of the proposed catalysts and on the physical and chemical characteristics (used as selection criteria) of all the substances involved. Promoters, or any other modifier or additive for the chosen catalyst, can be selected in a similar way.

Extensive information on the crystalline and electronic structure and on the physical and physicochemical properties of solids of stoichiometric composition is now available in standard handbooks. This allows us to choose as the selection criteria the most reliable data, determined by identical methods and under identical conditions, for the one-component catalysts. The most obvious choice of criteria includes the properties which are known (according to current theories of catalysis, or from experimental results) to be related to the ability of solids to accelerate chemical reactions. Some of these have already been discussed in Section II in relation to the use of simple correlation expressions for predicting catalyst behaviour. Some of the best known relationships between the catalytic activity and the physical characteristics of substances are discussed in Refs.6 and 18.

As well as experimental data, we can use as criteria the parameters of the electronic structure of solids, calculated by quantum mechanics or quantum chemistry methods, or various combinations of physical characteristics. Obviously, some of the properties of solids may be closely correlated, or even functionally related, if they have a common origin. The paramagnetism and the low-temperature specific heat of metals are typical examples; in the case of oxides the width of the forbidden energy gap is related to the colour and to other properties of the material. When choosing a system of criteria it is important to allow for these effects and to select characteristics which are as far as possible independent. The screening of superfluous (in this sense) properties can be made automatic by using the algorithms of mathematical statistics.

However, great care is needed in any preliminary statistical analysis of the system of criteria, because the exclusion of one or more members of a series of formally correlated properties may result in a serious lowering of the classifying and of the predictive power of the algorithm. This situation is illustrated in Fig.2, which shows a set of objects linearly separable in the space of two strongly correlated criteria (*A* and *B*). If one of these criteria is rejected the objects become unclassifiable by a simple binary classifier.

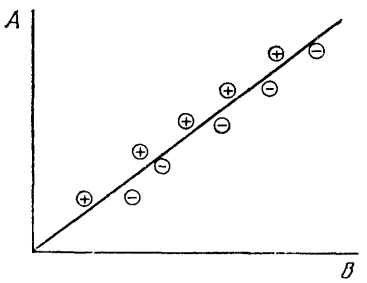


Figure 2. Examples of a linearly separable population in a space of correlated criteria *A* and *B*.

Even greater care is needed (for the same reason) in sifting the criteria on the grounds of weak correlation with the property of interest (catalytic activity, selectivity, etc.). It is intuitively obvious that some of the criteria may contribute only marginally to the catalytic activity towards certain reactions. These can be eliminated at the algorithm training stage, thus decreasing the number of dimensions of the recognition space. The "influence" of the criterion is a useful concept in this context. In the case of binary classifiers we can use as a measure of the influence the ratio

$$\beta_i = [\alpha_{cl} - \alpha_{cl}(i)]/\alpha_{cl}$$

where $\alpha_{cl}(i)$ is the classifying power of the algorithm in a space from which the *i*th criterion has been excluded. If the influence of the criterion is small, i.e. if its exclusion does not materially affect the classifying power, the criterion can legitimately be omitted.

The first reported use of recognition methods for catalyst prediction[39] dealt with the oxidation of CO on metal oxides, relying on the experimental information collected by Krylov[40]. The training sample consisted of 26 oxides: MoO_2, CoO, Co_3O_4, MnO, CdO, Ag_2O, NiO, CuO, SnO_2, Cu_2O, Co_2O_3, ZnO, TiO_2, Fe_2O_3, MgO, CeO_2, V_2O_5,, Cr_2O_3, ZrO_2, HgO, WO_3, ThO_2, BeO, GeO, Al_2O_3, and SiO_2. 20 physical properties of the catalysts, available in standard tabulations, were used as criteria. The catalysts were divided into three classes: good, moderately good, and poor, on the basis of their catalytic activity (listed in Ref.40). A success rate of 84% was achieved in the prediction for oxides taken out of the training sample by using successive dichotomies with a potential functions program[41]. By using methods to be discussed below it was shown that only 8 of the 20 criteria had any influence on the activity. Predictions of catalytic activity towards the oxidation of CO were made for a number of oxides not previously used in this reaction: in the case of HfO_2 the prediction was experimentally confirmed[42].

In the selection of a promoter for the catalytic formation of low-molecular aromatic hydrocarbons from alkanes of intermediate molecular weight (for example, dodecane) the training sample consisted of the oxides V_2O_5, MoO_3, CeO_2, Cr_2O_3, CaO, Bi_2O_3, and K_2O, which had been previously studied experimentally[29]. The objects for recognition included the oxides CoO, Mn_2O_3, CuO, Ag_2O, NiO, PdO, La_2O_3, ZrO_2, and WO_3.

Five "influential" properties were identified (Table 1) from the initial list of 12. Recognition was effected by the "Prognoz-73" program, using a two-category system. The validity of the prediction was tested experimentally, and the high activity which had been forecase for the oxides ZrO_2, Mn_2O_3, and WO_3 was confirmed.

Table 1. Physicochemical properties of oxide promoters[29].

Oxide	$Z(I+a)$	μ	r_M, (Å)	r_K, (Å)	n
V_2O_5	52.20	+128.00	0.91	0.80	0
MoO_3	51.72	+3.00	0.91	0.81	0
CeO_2	28.64	+26.00	0.94	0.99	0
K_2O	2.74	—29.00	1.39	1.08	0
CaO	9.60	—15.00	1.06	1.03	0
Bi_2O_3	23.88	—83.00	1.025	0.915	2
Cr_2O_3	28.59	+1 960.00	0.815	0.935	3
Ag_2O	8.23	—134.00	1.19	0.91	10
NiO	19.88	+660.00	0.875	0.95	6
CuO	20.00	+238.90	0.95	0.90	9
PbO	11.40	—42.00	1.11	0.935	2
Mn_2O_3	29.64	+14 100.00	0.81	0.945	4
La_2O_3	19.50	—78.00	1.04	0.99	0
ZrO_2	30.16	—13.80	0.88	0.94	0
WO_3	51.72	—15.80	0.91	0.82	0
CoO	18.58	+4 900.00	0.88	0.955	5

Symbols: Z is the valence of the metal, I is the ionisation potential (eV), a is the electron affinity (eV), μ is the magnetic susceptibility, r_M is the ionic radius of the metal, r_K is the ionic radius of the oxygen, n is the number of valence electrons not taking part in metal–oxygen bonds.

Table 2. Prediction of the promoting properties of elements added as oxides to vanadium–molybdenum catalysts[44].

Element	Δ_{exper}, %	Δ_{pred}, %	Element	Δ_{exper}, %	Δ_{pred}, %
Mg	35	32	Ce	—15	—11
Ti	5	11	Pr	10	6
Fe	—10	—8	Nd	5	10
Co	20	14	Gd	3	13
Ni	20	17	Tb	—3	2
Cu	—10	—8	Ho	10	14
Y	35	24	Er	20	10
Ag	—10	—7	Yb	35	13
Cd	3	4	Tl	—3	—4
La	3	13			

Symbols: experimental (Δ_{exper}) and predicted (Δ_{pred}) values of the change in the depth of oxidation of furfural caused by the addition of the promoter to the vanadium–molybdenum system.

A study[43] of the properties of the training sample of metallic promoters (consisting of metals from Groups VI and VII) has led to the prediction of a new, active promoter for nickel catalysts used in the hydrogenation of unsaturated compounds: niobium. The calculation was carried out with a potential functions program, using a three-category successive dichotomy scheme.

Promoters for multi-component vanadium–molybdenum catalysts used in the oxidation of furfural to maleic anhydride have been predicted[44]. The predictive experiments were organised as follows: out of 19 experimentally tested promoters, 17 were used to train the computer, and for the other 2 the selectivity of the reaction was predicted from the variation in the yield of side-products (resulting from full oxidation). An algorithm which forecasts the numerical value of the parameter of interest (in this case, the selectivity of the reaction) was used in this work. The algorithm, fully discussed in Ref. 44, consists in reproducing the shape of the function which describes the dependence of the selectivity on the physicochemical properties of the promoters. Effective criteria (and combinations of criteria) were chosen by an algorithm of the type used in Ref. 37. The results are shown in Table 2.

It is clear from Table 2 that the algorithm used in that work[44] had a high predictive power. Only four of the ten properties of the promoters arbitrarily selected were found to be effective: the distance between the metal atom and the oxygen atom, the electronegativity difference and the width of the energy gap in the oxide, and the colour of the oxide.

A factor analysis algorithm, based on the coefficients of the linear correlation between the output parameter Y (the logarithm of the exchange current) and a set of criteria chosen *a priori*, has been used[25] in the recognition and prediction of one-component metallic catalyst electrodes for electrolytic hydrogen evolution. The output parameter was defined by the expression

$$Y = \sum_{j=1}^{N} a_j \tilde{x}_j$$

where $\overline{x_j}$ are the average values of the normalised criterion, and a_j is a coefficient obtained by least squares. By using factor analysis for ranking the criteria[45] the initial set of seven criteria was reduced[25] to three: classifications based on these criteria (by the dichotomy method) agreed in 80% of the cases. The algorithm has also been used[26] to recalculate earlier results[39]: it gave a slightly worse agreement (80% instead of 84%), probably because the postulated linear dependence of the property of interest on each of the criteria is too rough an approximation. This work[25,26] shows that the factor analysis algorithms can be useful for catalyst recognition and prediction, though their power is lower than that of the "pure" recognition algorithms and their validity is more limited.

IV. PREDICTION OF MULTI-COMPONENT CATALYSTS

The most difficult (and yet, perhaps, the most important) problem of this type is the use of recognition methods in predicting multi-component catalysts at the component selection stage, i.e. when the true physicochemical properties of the working catalyst are still unknown. The only possible approach is to use the properties of the components used in the synthesis of the catalyst. Two paths are available: either to seek an effective method of calculating the physicochemical properties of multi-component solids, thus reducing the problem to the use of algorithms adequate for one-component catalysts, or to construct multi-level heuristic programs in which the recognition programs appear as sub-programs[46].

The simplest approach[21,22] to the prediction of multi-component catalysts relies exclusively on chemical composition data, using the following algorithm. The catalysts are classified into two opposite groups: one group catalyses the reaction for which a prediction is required, while the other group catalyses a reaction with the opposite mechanism. The identification (assigned to a class) problem is solved geometrically. The total set of initial data used as a training sample forms a matrix having $(M \cdot N)$ dimensions, where M is the number of objects and N is the number of criteria (in the

form of zeros and unities). In a row describing an object an entry of 1 denotes the presence in the object of a particular element. Standards are chosen for each class, and these act as "centres of gravity" for the class in N-dimensional criterion space. The object is considered to belong to one of the classes if its Euclidean distance from the standard for that class is less than the distance from the standard of the other class. The closer the unknown object is to the standard of the class of interest, and the further from the standard of the other class, the better are its prospects. A linear relationship between the activity of the catalyst and its geometric criterion (defined above) was demonstrated, as well as a high (>90%) probability of correct assessment of the activity or selectivity of catalysts.

An obvious disadvantage of this approach is that the search for possible new variants of catalysts is limited to elemental composition, since this is the only variable parameter in the training sample.

A more systematic approach to the prediction of multicomponent catalysts relies on a preliminary calculation of the physicochemical characteristics of the catalysts from data relating to the components. This type of problem is not uncommon in solid state chemistry, and it can be solved in a number of ways[47–49], all based on interpolation relationships in which the properties of the components are somehow averaged. Modern theories of the electronic structure of disordered solids also rely on this approach, though not always explicitly[50].

The use as criteria of quantities calculated by interpolation formulae offers two important advantages. One, already mentioned above, is the possibility of exploiting the extensive data available for one-component catalysts in predictions of multi-component catalysts. The other advantage is the very attractive possibility of predicting the properties of catalysts of complex composition from data on the catalytic properties of pure metals, oxides, etc.

The simplest way of averaging is with respect to mole fractions. In spite of its roughness this method is found experimentally to be useful for tentative predictions. It has been applied[29] in the prediction of the activity of mixed oxide catalysts for the aromatisation of the lower alkanes (the first step in the selection of a catalyst for the preparation of a "low aromatic" fraction from alkanes of moderately high molecular weight, described above). The correlations between the catalytic activity and the electronic and structural properties of the mixed oxide catalysts were established by the potential functions method. The catalytic activity was quantified (in terms of the selectivity s) from the total yield of aromatic compounds for the very large number of mixed dehydrocyclisation catalysts described in the literature, using the three-class system

class I ("good"): $67 < s < 100$
class II ("fairly good"): $33 < s < 67$
class III ("poor"): $0 < s < 33$

The effect of the energy of electron vacancies in the active centres and of the defect structure of the catalyst surface was calculated by the function

$$Q = \frac{\sum \nu_i [Z_i (I_1 + a)_i]}{1 + \bar{\mu}}$$

where ν_i is the mole fraction of the component in the mixture of oxides, Z_i is the valence of the metal in the ith oxide, and $(I_1 + a)$ is the sum of the first ionisation potential and of the electron affinity of the metal in the ith oxide. The numerator of the fraction is a measure of the acidity of the catalyst. The parameter $\bar{\mu}$ is the crystal-chemical similarity of the components of the oxide mixture, expressed on a point scale, which determines the defect structure of the surface. The averaged value of the magnetic susceptibility ($\bar{\chi}_\mu$) was used as the second criterion.

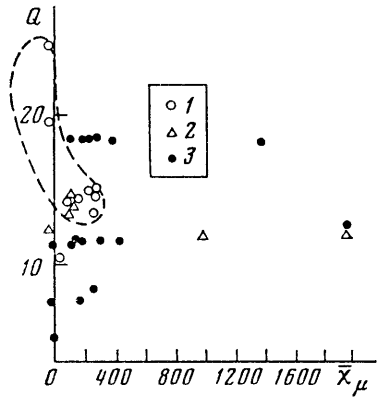


Figure 3. Distribution in criterion space of the catalysts for the aromatisation of the lower alkanes: *1*) good, *2*) average, *3*) poor catalysts.

It is clear from Fig.3 that in spite of the rough approximation of the initial assumptions the catalysts are well classified into three groups, even in two-dimensional space.

Other reactions have been studied on mixed oxide catalysts, including the hydrogenation of compounds with an ester group to alcohols and the gas-phase conversion of formaldehyde and isobutene into isoprene[27]. Owing to the lack of strict methods of calculating the characteristics of the electronic structure of mixed solid-phase systems there is no alternative to using an approximate additive scheme to obtain the properties of the mixed oxide catalyst: the property X is expressed as $X = \sum_i x_i \nu_i$, where x_i is the property for the pure component i and ν_i is its mole fraction. The following combinations of properties were identified as the most effective for catalysts used in these processes. For the hydrogenation of esters, $\sum_i (n_{d,f} + N_{d,f})_i \nu_i$ (where $n_{d,f}$ is the number of d and f valence electrons not taking part in bond formation with the oxygen, and $N_{d,f}$ is the number of fully occupied d and f shells in the metal atom) and $\sum_k J_k \nu_k$, an average value of the bond ionicity, and for the conversion of formaldehyde the average magnetic susceptibility $\sum \chi_i \nu_i$ and the parameter $\sum_k J_k$ (the sum of the bond ionicities in the active components).

Thus only two properties were found to be effective for each of these processes, and therefore the assignment to classes in property space can be displayed graphically (Fig.4). A separation is achieved, but we note some overlap of the classes (due to the lack of precision of the additive scheme used to calculate the properties).

Since many physical and chemical properties are not additive even in systems consisting of chemically similar components much care is needed in selecting the recognition criteria when averaging procedures are used. The most convenient and valid approach appears to be the use of microscopic characteristics, i.e. atomic parameters. Averaged

values of the atomic parameters, though physically meaningless, are often very accurately correlated to the properties of multi-component systems. Thus averaged values of the ionisation potential and of the electron affinity can be correlated with the work function of alloys, averaged radii with the molar volume, etc.

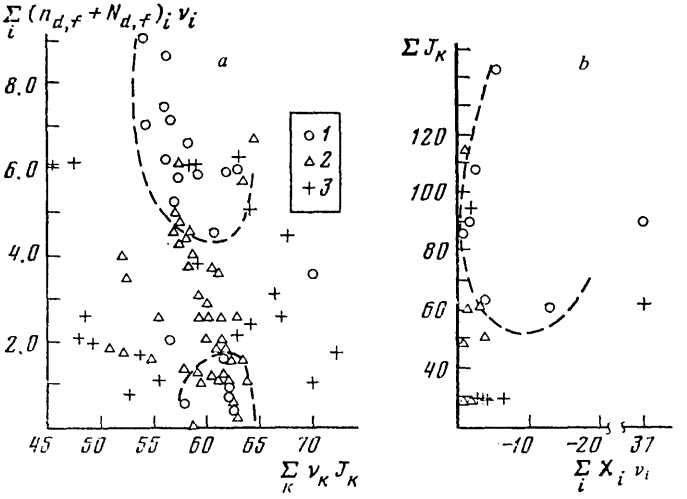


Figure 4. Distribution in criterion space of the catalysts for the hydrogenation of esters (*a*) and for the conversion of formaldehyde/isobutene into isoprene (*b*). Points *1–3* as in Fig. 3.

We have used averaged atomic parameters[28] as criteria for predicting hydrogen peroxide decomposition catalysts by a linear binary classifier with a non-zero threshold. The training sequence consisted of 93 alloys of silver or gold with Group VIII metals, for which catalytic activity data are given in a recent review[51]. The proportion of correctly classified catalysts was 85%, which appears to be the highest success rate which this algorithm can offer. Predictions were attempted for 38 catalysts. The predictive power of the algorithm was found to be slightly lower than the classifying power (80%).

The next improvement in the system of criteria is the replacement of atomic by averaged orbital characteristics, corresponding to the electrons in the valence sub-shells of the atoms. These include the quantum numbers, the orbital ionisation potentials, the average orbital radii, etc. Average values of whole classes of some of these characteristics can also be used as criteria. This allows us on the one hand to adopt a more flexible training program, since it can be shown[35] that the use of these characteristics is equivalent to changing from a linear classifier to one of a higher order. On the other hand the use of averages of a class of criteria (i.e. the moments of the criteria) justifies the departure from a purely additive scheme in the calculation of the parameters of multi-component catalysts.

The general formula for calculating the criteria thus becomes

$$X_{n\alpha} = \sum_i \nu_i \sum_j c_{ij\alpha} x_{ij}^n$$

where ν_i is the atom fraction of the *i*th component, *j* is the number of valence sub-shells, $c_{ij\alpha}$ is a weighting coefficient for averaging with respect to orbitals, and α is an index denoting the method of averaging used. This index is used because the orbital parameters for the atoms of each component can be averaged in different ways: over the number of orbitals in the valence sub-shells or over the number of valence electrons in the sub-shells (i.e. for the occupancy of the sub-shells, and hence also the number of unoccupied states ("holes")). All these methods of averaging give mutually independent results, with a different physical meaning.

Table 3. Classification, criteria, and level of influence of the criteria for bimetallic hydrogen peroxide decomposition catalysts.

[M], at.%	Activity, arbitrary units	Criteria				
		I (−0.387)	II (−0.375)	III (−0.349)	IV (−0.344)	V (+0.266)
		High activity				
15 Ir	2.971	64.319	7.998	488.54	524.41	0.470
11 Rh	2.371	63.317	7.920	504.85	540.84	0.364
11 Pt	2.114	62.770	7.895	498.89	533.15	0.200
25 Ru *	1.509	75.337	8.654	399.04	418.16	0.857
40 Os	1.486	63.728	7.970	379.28	423.74	1.091
40 Os *	1.463	76.221	8.705	376.20	399.04	0.750
25 Ru	1.386	62.908	7.917	466.26	506.97	0.857
		Low activity				
95 Rh *	0.314	79.465	8.860	405.17	420.04	1.312
92 Rh	0.314	78.706	8.816	412.17	431.47	1.294
78 Rh *	0.286	79.957	8.891	407.92	424.24	1.217
33 Pd	0.171	71.038	8.322	498.14	531.76	0.500
33 Pt	0.100	70.969	8.382	460.96	491.02	0.500
		Not classified				
17 Ir *	1.900	82.878	9.100	410.02	425.93	0.501
25 Pt	0.200	68.237	8.220	475.02	506.83	0.400

Symbols (criteria): I) square of the valance orbital ionisation potential (VOIP) of the neutral atom averaged over the unoccupied states of the valence sub-shells; II) VOIP of the neutral atom averaged over the unoccupied states of the valance sub-shells; III) square of the VOIP of the positively charged ion (+1) averaged over the number of atomic orbitals in the sub-shells; IV) square of the VOIP of the positively charged ion (+1) averaged over the number of valance electrons in the sub-shells; V) orbital quantum number averaged over the unoccupied states in the valence sub-shells. The level of influence of the criteria is shown in brackets.

*Au–M alloys; all the other alloys are Ag–M.

We have tested a system of 54 orbital criteria by producing a new set of predictions for the hydrogen peroxide decomposition catalysts mentioned above. Using the same algorithm, we raised its classifying power to 94.5% and its predictive power to 97.4%. Table 3 lists the most influential criteria for some of the compositions used in the classification, and Table 4 gives the corresponding values for the catalysts whose activity was predicted.

The use of orbital parameters as criteria in recognition algorithms brings the statistical approach closer to the methods of quantum mechanics and quantum chemistry, since those parameters are used in the calculation of the electronic structure of solids. Further progress in this direction can

be expected. Thus it should be possible to express the structure of multi-component catalysts by the procedures used in the cluster component method[48,49], i.e. to characterise the catalyst in terms of a set of lattice fragments (clusters) corresponding to different types of lattice site. In this representation the formula of an ideal binary crystal with an NaCl type lattice becomes $[AB_6]_{1/2}[BA_6]_{1/2}$, whereas an ideal substitutional solution with the same lattice and the same proportion of components is described by the formula

$$[AA_6]_{\nu_6^A}[AA_5B]_{\nu_5^A}[AA_4B_2]_{\nu_4^A}\ldots[BB_6]_{\nu_6^B}[BB_5A]_{\nu_5^B}\ldots$$

where ν_i^A and ν_i^B are calculated by assuming a random distribution of the two types of atom over the lattice sites. Averaged values of the parameters of the electronic structure of the clusters, calculated by quantum-chemical methods, can conveniently be used as criteria for the multi-component system. The averaging over the cluster components of a whole series of electronic structure characteristics (local densities of states, their moments, atomic contributions to the total energy, etc.) could have real physical significance, since these characteristics are strictly additive.

Table 4. Prediction of bimetallic hydrogen peroxide decomposition catalysts.

{M}, at.%	Criteria				
	I	II	III	IV	V
			High activity		
52 Ru *	70.710	8.386	372.06	391.6	1.219
56 Os *	69.448	8.312	296.15	318.84	1.254
29 Ir *	81.281	9.011	399.28	415.22	0.734
76 Ru	66.393	8.133	368.49	395.05	1.390
72 Os	65.355	8.071	283.56	311.20	1.367
32 Ir	68.491	8.280	457.27	491.29	0.780
12 Pt	63.161	7.918	497.33	531.49	0.214
			Low activity		
75 Rh *	80.047	8.897	408.52	424.89	1.200
57 Rh	74.922	8.595	450.92	481.41	1.065
34 Pd	71.244	8.334	497.74	531.30	0.507
71 Pt	80.00	8.919	400.12	419.76	0.830
			Incorrect prediction		
14 Rh	64.539	7.991	501.40	537.31	0.438

Note: the criteria and their influence are as defined in Table 3.

*Au–M alloys; all the other alloys are Ag–M.

So far in our discussion we have treated multi-component catalysts as fairly homogeneous solids (effectively single-phase systems). In fact, a large group of industrial catalysts has a more complex structure, and must be treated as multi-phase systems. The most important members of this group are the supported catalysts, consisting of an active metal phase and a carrier. In spite of their greater complexity, their catalytic properties can be predicted by the methods discussed here. The only new requirement is for a unified criterion space, including the properties of the carrier and of the support phase. The properties of each phase separately can be calculated by averaging.

As an alternative to averaging, we can approach the problem of multi-component catalyst prediction by constructing multi-level heuristic programs[46]. This possibility was tested[9,22] by applying the "Prognoz-76" program to the set of data on catalysts for the oxidation of 2,6-dimethylpyridine to 2,6-pyridinedialdehyde. The program was based on the following algorithm. The first stage consists in classifying the objects of the training sample according to the amount of components, using the "Prognoz-73" program. In the second stage the same program is used to identify the influential conjunctions of component properties which determine the assignment of the catalyst to class A. At this stage a distinction is made between the main components, present in all catalysts of classes A and B, and the promoters. In the third stage the substances possessing criteria similar to those of the components of class A catalysts are selected. In the last stage consisting of components with the required criteria in the optimum relative amounts (as determined in the first stage) is synthesised.

We should stress that methods of predicting multi-component catalysts are not yet fully developed. Further tests are needed before syntactic algorithms can be used to rationalise the combination of components with different properties into a single complex catalyst. The initial "words" for the grammar of syntactic algorithms of this type could be provided by the proposed[6] scheme of logic attributes of a good catalyst, such as activity of the components in side-reactions, type of adsorption, influence of promoters on the geometry of the crystal lattice of the catalyst, etc. However, in computer-aided recognition schemes the predictive power of this scheme is enhanced by the presence within each logic unit of quantitative information from the data banks, which facilitates the gearing of logic couplings.

V. ANALYSIS OF CATALYTIC ACTION MECHANISMS (THE INVERSE RECOGNITION PROBLEM)

Pattern recognition methods can be used not only in the prediction and classification of catalysts, but also as an effective means of analysing the mechanism of catalytic reactions. For this purpose we use the "inverse pattern recognition problem", whose goal is not the prediction of new catalysts but the study and the ranking of the properties of catalysts, reactants, and products (in so far as they affect the rate and the selectivity of the stated reaction). By identifying these products and relating them semi-quantitatively to the output parameters of the reaction the investigator can acquire a basis for a theoretical model of the catalytic reaction and of the relationships between its mechanism and the structure of the reactant and product molecules. Stricter functional dependences can be obtained from the sem-quantitative relationships. The data required for analysing catalytic action mechanisms follow directly from the method of solving the prediction problem, and can be considered to be incidental results. This is because all recognition algorithms contain some provision for minimising the number of dimensions of the problem, i.e. for "rejecting" unimportant criteria, so that the criteria are ranked in terms of their influence on the output parameters of the objects.

Several algorithms for ranking the criteria and minimising their number have been used in the solution of catalysis problems. In the potential functions methods a simple "sliding recognition" algorithm (involving repeated recognition) has been effective. Each criterion is omitted in turn from the initial sample: if the success rate of the recognition is unchanged (or increased) by this omission the criterion is excluded from all further calculations. The other criteria (or properties) are ranked according to their contribution to the success of the recognition.

The pattern recognition problem for CO oxidation catalysts was solved by taking an initial set of 26 properties[39]. However, by using the sliding recognition algorithm the number of criteria was decreased to eight. We note that only four of these could be related to the catalytic activity by correlation analysis methods with a probability greater than 95%. The other criteria, taken singly, showed practically no correlation with the catalytic activity: this shows the importance of combinations of properties in creating an effective solid catlyst, as well as underlining the limitations of the predictive power of correlation methods in one dimension (or in a few dimensions).

Table 5. Results of the computer recognition of the selectivity of oxidation reactions on a V_2O_5 catalyst[41].

No.	Initial compound	Final compound	Success of prediction
	Class A (selectivity greater than 50%)		
1	*o*-Xylene	Phthalic anhydride	+
2	Naphthalene	Phthalic anhydride	+
3	Anthracene	Anthraquinone	+
4	Toluene	Benzoic acid	+
	Class B (selectivity between 50 and 10%)		
1	*m*-Xylene	Maleic anhydride	+
2	Pent-1-ene	Acetaldehyde	–
3	Pent-2-ene	Acetaldehyde	–
4	Butadiene	Maleic anhydride	+
5	Naphthalene	1,4-Naphthylquinone	+
6	Anthracene	Phthalic anhydride	+
7	*p*-Xylene	Maleic anhydride	+
8	*p*-Xylene	*p*-Toluic anhydride	+
9	*p*-Xylene	Terephthalic anhydride	+
10	2-Methylbut-2-ene	Acetone	+
11	*m*-Xylene	*m*-Toluic aldehyde	+
12	Toluene	Benzaldehyde	+
13	2-Methylbut-2-ene	Acetaldehyde	+
14	2-Methylbut-1-ene	Acetone	+
15	2-Methylbut-2-ene	2,3-Epoxy-2-methylbutene	–
16	2-Methylbut-1-ene	Acetaldehyde	+
17	But-1-ene	Maleic anhydride	+
18	But-2-ene	Maleic anhydride	+
19	3-Methylbut-1-ene	Acetone	+
20	Pent-1-ene	Acetone	+
21	Pent-2-ene	Propionaldehyde	–
22	Pent-2-ene	Methanol	–
23	2-Methylbut-2-ene	3-Methylbutan-2-one	–
	Class C (selectivity less than 10%)		
1	Propene	Formaldehyde	–
2	Pent-1-ene	Butanol	+
3	2-Methylbut-1-ene	2,3-Epoxy-2-methylbutane	+
4	Pent-2-ene	2,3-Epoxypentane	+
5	2-Methylbut-1-ene	Butanol	+
6	3-Methylbut-2-ene	Acetaldehyde	+
7	Pent-1-ene	Propionaldehyde	+
8	Pent-1-ene	Butyraldehyde	+
9	Pent-2-ene	2,3-Epoxypentane	+
10	Pent-1-ene	Methanol	+
11	Pent-1-ene	Crotonaldehyde	+
12	3-Methylbut-1-ene	Butanol	+
13	Propene	Acetaldehyde	+
14	Pent-2-ene	Butanol	+
15	Pent-2-ene	Acetone	–
16	2-Methylbutene	2,3-Epoxy-2-methylbutane	+
17	*p*-Xylene	*p*-Toluic acid	–
18	Butadiene	Formaldehyde	–
19	3-Methylbutane	3-Methylbutan-2-one	+
20	Pent-2-ene	Butan-2-ol	+
21	2-Methylbut-2-ene	Butanol	+
22	Pent-2-ene	Ethanol	+

In the "Prognoz-73" program the level of influence of the criteria is measured by the frequency with which a criterion occurs in the conjunctions of criteria leading to recognition. By using this algorithm we were able to lower the number of influential properties of the reactant and product molecules from 46 to five or six in the prediction of the selectivity of the oxidation of hydrocarbons on vanadium pentoxide. The problem was specially formulated to clarify the mechanism of oxidative conversions. The training sample consisted of a set of data[52,53] on the selectivity of the partial oxidation on vanadium pentoxide of more than 50 hydrocarbons. The results of the recognition experiment (Table 5) show a high proportion of successes, and therefore they confirm the validity of conclusions on the influence of the properties of reactant and product molecules on the selectivity of the reaction.

The properties of the reactants, catalysts, and products which affect the rate and the selectivity of the oxidation of hydrocarbons most markedly can be listed as follows. For the hydrocarbons being oxidised the properties (in decreasing order of influence) include: 1) the ionisation potential, 2) the number of symmetry operations, 3) the free valency index, 4) the magnetic susceptibility, 5) the dipole moment, 6) the steric accessibility of the C–C bond with maximum structural correspondence. For the oxidation products we have: 1) the π-electron density, 2) the highest π-electron level, 3) the ionisation potential, 4) maximum structural correspondence between the C–C bond and the crystal lattice of the catalyst, 5) steric accessibility of the C–C bond with maximum structural correspondence.

The most influential properties of the catalysts for the oxidation of carbon monoxide can be arranged in the following sequence: 1) density, 2) colour, 3) melting point, 4) ratio of the volume of the crystallographic holes in the oxide to the volume of the metal atom, 5) width of the forbidden energy gap, 6) molar magnetic susceptibility, 7) number of *d* electrons not involved in bond formation between metal and oxygen, 8) ionisation potential of the metal atom (averaged for the valence of the metal in the catalyst). The effective properties of the promoters[44] for vanadium–molybdenum catalysts used in the oxidation of furfural can also be listed (though the relative magnitude of their influence has not yet been determined): 1) distance between metal and oxygen atoms in the oxide, 2) electronegativity difference in the oxide, 3) width of the forbidden energy gap, 4) colour. Similarly, for the oxidation of dimethylpyridine: 1) width of the forbidden gap, 2) ionisation potential of the metal atom, 3) ratio of the volume of the crystallographic holes in the oxide to the volume of the metal atom, and 4) coordination number of the metal atom in the crystal lattice of the oxide.

These results allow us to make some general conclusions on the mechanism of oxidation reactions on heterogeneous catalysts, and can be used as evidence for the general validity of the inverse recognition problem.

The properties of the catalysts, and those of the organic molecules, can be classified into two groups: electronic and geometric. The selectivity of the oxidation reactions (i.e. the ratio of the rates for different reaction paths on the given catalyst) is a function of a combination of properties of both the reactant and the product molecules.

Let us examine more closely the electronic properties group of the solid. They all affect the mobility of the electrons in the solid, which is ultimately determined by the excitation energy of the electrons. These properites can be treated as enthalpic properties of the catalyst, which determine the activation energy of the reaction. The factors which affect the mobility of the electrons can themselves be divided into two groups: individual (determined by the electronic configuration of the metal atom, i.e. the ionisation potential, number of free *d*-electrons, etc.), and collective (electron density, width of the energy gap, colour, magnetic susceptibility). The latter group of properties includes also the melting point, which varies in the same sense as the energy of the interatomic

bonds in the lattice and therefore characterises the ease of "unpairing" of electrons in these bonds (in particular, the metal–oxygen bonds), and also the probability of forming lattice defects.

Thus, in contrast to the narrow view that catalytic properties result either from the local or from the collective properties of solids our analysis shows that the formation of an effective catalyst requires a combination of both types of property.

In addition to the electronic properties, the group of influential properties of catalysts includes parameters which characterise the geometry of the lattice: the ratio of the volume of the holes to the volume of the metal atom, and the distance between the metal and the oxygen atoms in the oxide. The mechanism of action of these parameters can be related both to the structural correspondence between the lattice of the catalyst and the organic molecule and to the ease of diffusion of oxygen atoms from the bulk to the surface, which can be very important in the partial oxidation of organic compounds.

Let us now turn to the properties of the organic molecules (reactants and products). The properties which affect the selectivity of the reaction now include the ionisation potential, the π-electron density and the π-electron level, the magnetic susceptibility, and the free valency index. This is not surprising, since the rate and the selectivity of the oxidation reaction are ultimately determined by electron transfer processes in the reactant–catalyst–product system.

Consider now the geometric properties of the organic molecules which are found to be influential. On the whole, their correlation with the mechanism of the catalytic action is self-evident: steric accessibility of the bond and maximum structural correspondence between the C–C bond and the lattice of the catalyst The importance of the number of symmetry operations of the reacting molecule is not coincidental: the influence of this factor arises from the increased probability of interaction between the reacting molecule and the catalyst surface, since interaction occurs during any type of collision if the molecule is symmetrical. The presence of a dipole moment in the molecule also increases the probability of effective collision by orienting the incident molecule in the electrostatic field of the catalyst. It is interesting to note that this analysis fully confirms Balandin's principle of geometric correspondence in heterogeneous catalysis.

We should also stress another result, which is often ignored. In order to show good selectivity a catalytic reaction requires a definite correspondence in the combination of properties not only between the reactant and the catalyst but also between the reactant ("substrate") and the product. Thus in the separation of the above set of hydrocarbon oxidation reactions into two classes with a selectivity threshold of 25% different criteria of the reactants and the products are found to be influential (Table 6), but their interplay is logical and easily interpreted. Clearly, a hydrocarbon of class A must be a good electron donor, and therefore it should have a low ionisation potential and a well delocalised system of π-electrons (a low minimum free valency index according to Coulson). Correspondingly, the reaction product should be stable, i.e. it should be a poor electron donor (with a high ionisation potential) and it should not have a highly developed π-electron system (in order to facilitate desorption of the product).

For the class B hydrocarbons we expect the opposite properties, as well as a high structural correspondence between the C–C bond of the reaction product and the oxygen of the lattice, which favours breakdown of the product molecule. It can be shown that the predominant properties (and their relative values) for the product and the reactant vary with the value of the threshold chosen for the classification.

This example of the analysis of a reaction mechanism has established that the effectiveness of the catalytic act in the oxidation of hydrocarbons depends on a favourable conjunction of two types of factor: enthalpic (related to the energetics of the electronic transitions) and entropic (related to the geometry and symmetry of the molecules and of the lattice). The catalyst, reactant, and product make equally important contributions to the process, and the outcome is determined by an appropriate combination of their properties.

Table 6. Combinations of properties in molecules which determine the selectivity of the reaction.

Molecule	Properties	
	Class A ("good")	Class B ("poor")
Oxidised hydrocarbon	Low value of I, low value of κ	high value of κ
Oxidation product	High value of I, optimum ρ_π, high value of ΔE	high level of structural correspondence between the C–C bond and the O-atom of the catalyst, high value of ρ_π, low value of ΔE

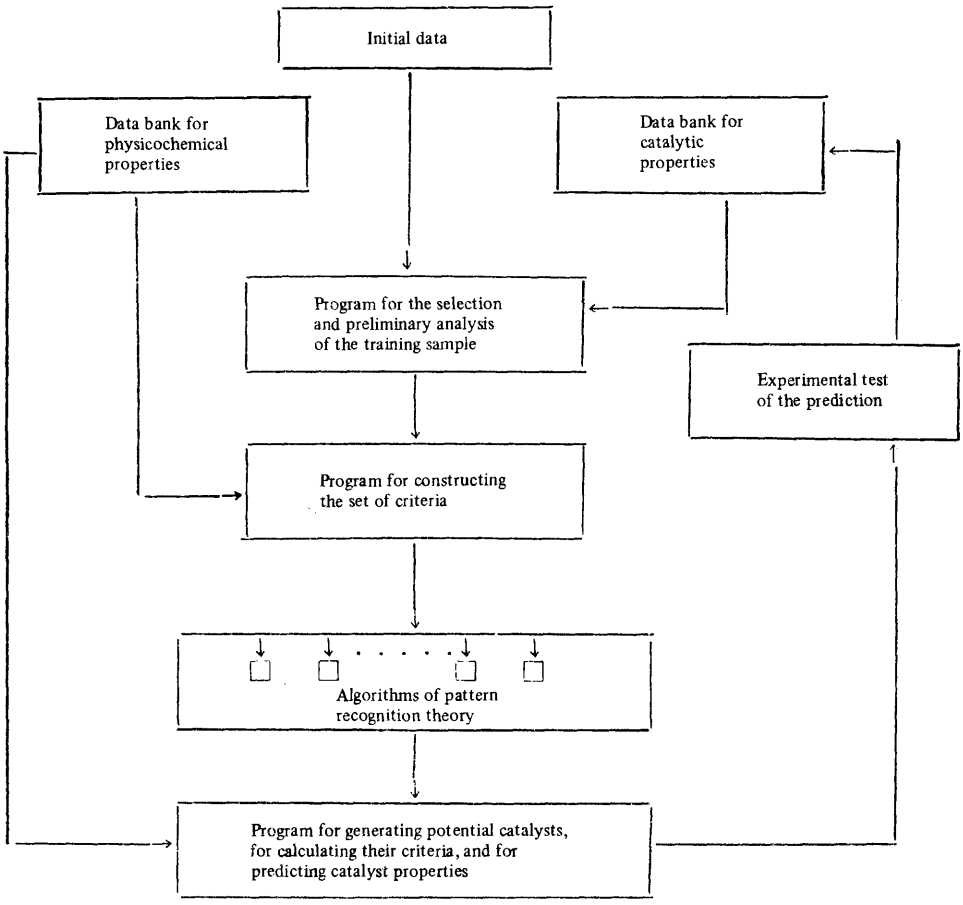
Symbols: I ionisation potential, κ minimum free valence index (Coulson), ρ_π minimum π-electron density, ΔE difference between the sums of the dissociation energies of the initial and the final compound.

VI. PROSPECTS OF FUTURE DEVELOPMENTS

Pattern recognition theory was formulated as a new topic in applied mathematics towards the end of the 1950's, but its practical application in science and technology had to await the development (in the 1960's) of the second generation of computers, which made the laborious calculations involved a practical possibility. The earliest applications of recognition methods to catalyst prediction were reported during that period. However, until specially adapted computational methods became available the problem remained intractable because it tended to make unreasonable demands on computer time.

The appearance and wide adoption in the 1970's of third-generation computers offered entirely new possibilities of automating all the steps in the prediction of catalyst behaviour by pattern recognition methods, including the choice of components of the training sequence, the search for and calculation of the physical properties, etc., and also the automatic "splicing" of all the steps. An efficient way of exploiting these possibilities is to set up an automatic system for predictions by pattern recognition methods, consisting of data banks, problem modules, and training programs. The significance of these concepts will be explained below: at this point we shall only stress the fact that the work which initially had to be done manually is now handled by the algorithms of the system.

The most general type of system for the prediction of heterogeneous catalysts is illustrated in the diagram. Without entering into its details, we shall examine the basic principles which should be borne in mind when designing a system of this type.



The first step in the creation of such a system is the organisation of renewable data banks, i.e. tables of properties, stored in the archives of the external memory of the computer. One of these should contain data on the state of the catalysts, their activity and selectivity, and other "desired" properties, while the other is dedicated to data on the physicochemical properties of solids. As stated above, a comprehensive and well documented handbook on catalyst properties is now available[18], with regularly published supplements. This can provide the basis of the catalyst data bank, to be updated as new information becomes available.

An important consideration in the assembly of the catalyst data bank is the reliability of the initial data. In any recognition algorithm the inclusion of unreliable data in the training sample must lower the validity of the prediction. Unfortunately, in the field of catalysis unreliable data are especially numerous, with many deliberately misleading ("diversionary") data in open publications as well as in patent applications. To some extent this can be guarded against by introducing weighted reliability coefficients: for example, 1 for original and well substantiated data in reputable publications, 0.8 for other publications, and 0.5 for patents. Allowance for the reliability coefficients can be made in the training of the recognition algorithm. Thus if the potential functions method is used the contributions of the objects to the total potentials of the classes are simply multiplied by the appropriate reliability coefficient. Other methods of allowing for the reliability of the data either directly or indirectly are available for the other algorithms.

The physicochemical properties bank should include data on a wide range of solids of various classes. The choice of these properties is a fundamental problem in the development and application of recognition methods. At present it is helpful to subdivide the criteria into two classes (basic, and derived). Since chemical reactions take place at the atomic–molecular level the basic criteria should include data on the crystallographic and electronic characteristics of the catalysts, and also on the atoms of their constituent elements. The criteria should be, as far as possible, quantitative, though the use of qualitative characteristics (of the "yes" or "no" type) is not excluded.

Criteria related to the electronic structure of solids (width of the energy bands, Fermi level, electron density and density of states, strength of interatomic bonds, etc.) determine the energetics of the chemisorption and of the overall catalytic act. In this sense they can be termed enthalpic. The geometric parameters of the crystal lattice (in particular, its symmetry) can influence the probability of various elementary acts, i.e. they can determine the entropy factor, as well as being naturally related to the electronic structure.

The derivative criteria are obtained by functional relationships from the basic criteria. Practically any of the physical properties of solids can be used as an example. Thus the density is related to the crystal lattice parameters and to the composition of the substance, the depth of colour to the width of the forbidden energy gap, etc. Supplementing the

basic criteria with derived criteria can be helpful in the solution of the inverse recognition problem.

The first step in the operation of a prediction system is to search the catalyst bank for catalysts which accelerate the reaction of interest and to classify them according to activity (or other specified property), number of phases (presence of a carrier, etc.), and chemical composition. These catalysts are the training sample. If the bank contains few data (or no data) on the reaction under study a sample of reasonable size can nevertheless be assembled by using data for analogous reactions[27,29].

In the next step the properties of the components of the catalysts in the training sample are extracted from the bank of physicochemical properties. These are used to generate the criteria to be applied in the recognition. The formulation of these criteria may require special calculations (for example, quantum-chemical), and therefore this part of the system may include a whole set of programs. Before compiling tables of criteria it is advisable to sift out the criteria which are mutually correlated. Superfluous criteria can be excluded by ranking them according to their influence, using the fastest (though not necessarily the most effective) recognition algorithm. These algorithms can be termed first-level algorithms. They can conveniently be realised by using the programs of the potential functions method.

When the required correspondence between the size of the training sample and the number of criteria has been achieved, the main step in the operation of the system can take place: the training of the second-level recognition algorithms. The purpose of this step is to find the optimum recognition procedure, offering the highest classifying power. If the required classifying power cannot be achieved by any of the algorithms we must go back to the criterion formulation step and find additional criteria (and criterion correlations).

When a classifier offering an acceptable effectiveness has been defined, a prediction of the target property can be made for all the proposed objects. In the previous methods of prediction the target properties were listed by the experimenter, but the automated scheme includes a block which generates possible compositions of (hypothetical) effective catalysts. This block operates in two steps. At first, by using repeated dichotomies or other decision processes, it outlines a region of effective criterion space corresponding to the optimum value of the catalyst property of interest. Then it generates hypothetical catalysts whose criteria lie within the selected region. In the case of one-component catalysts or promoters this is equivalent to choosing from the catalyst bank the compounds with the most favourable set of properties. In the case of multi-component catalysts the system identifies combinations of substances having criteria close to the optimum values.

If the dependence of the physicochemical properties of the catalysts on the concentration of the components can be described by a simple functional relationship (for example, some form of averaging) the problem of finding the best composition can be formulated mathematically as the search for a minimum in some function of the composition. The most obvious choice of this function is the sum of the squared deviations of the criteria for the chosen catalysts from their optimum value:

$$\Phi(\nu) = \sum_i \rho_i [\chi_{oi} - \chi_i(\nu)]^2$$

The weighting coefficients ρ_i reflect the degree of influence of the criterion. The final result from the operation of this system is a recommendation of the relative amounts of active components likely to yield the best catalyst or promoter.

The results of experimental tests of the predictions can be used to supplement the catalytic properties bank. If a catalyst offering the required effectiveness has still not been found, a new prediction is made with the expanded data bank, and the search becomes an iterative procedure. In this variant the pattern recognition method can be used for planning experiments on catalyst selection when the initial information is insufficient for "training" the computer[9].

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Study of the Acid-Base Properties of Heterogeneous Catalysts by Infrared Spectroscopy

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The quantitative assessment of the acid-base properties of the surface of heterogeneous catalysts by i.r. spectral studies of adsorbed molecules is discussed. The quantities through which the protonic (Brønsted), aprotic (Lewis), acidic and basic centres of the surface can be most easily characterised are analysed. Reported methods of determining the number and strength of the surface centres are described. 135 references.

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I. INTRODUCTION

Solid acids and bases are widely used to catalyse various reactions at the solid-gas or solid-liquid interface. In order to understand the mechanism of their catalytic action and to predict their activity and selectivity we need quantitative information on the number and strength of the acid or basic centres on their surface[1-3]. In the 1950's the indicator method of determining the strength of the acid centres[4] and the indicator titration method of determining their number[5] were proposed: both these methods were based on a study of the interaction of indicator molecules (probes) with the surface. More recently similar methods have been used to characterise basic centres[6,7].

The physicochemical foundation of these methods of quantitative assessment was the postulate that the interaction between the acid centres on the surface and bases from the external phase is analogous to acid-base equilibria in solutions. However, some differences in principle between solid acids (or bases) and acids or bases in solution were subsequently discovered. On a surface we find, at the same time, fixed, non-interacting acid centres (aprotic, L, and protonic, OH) and basic centres (B_S), of different strengths. This gives rise to independent, parallel reactions, seldom reaching equilibrium, between the added (probe) molecules and the surface centres. Under these conditions the above methods[4-7] cannot give the true characteristics of the acid–base properties of specified surface centres.

Some attempts[2,8] to develop more realistic methods of studying the acid-base properties of surfaces proved unsuccessful. However, they led to the formulation of the following list of requirements to be met by a successful quantitative method: 1) the interactions between the probe molecules and the protonic, aprotic, and basic centres should be

Table 1. Acidic and basic surface centres, and requirements on the probe molecules used to study them by i.r. spectroscopy.

Type of centre	Lewis (L) centres	Brønsted (OH) centres		Basic (B_S) centres
Type of complex with probe	donor-acceptor complex	H-bond	ion pair	H-bond
Spectral criterion of complex formation	change in frequency of the characteristic vibrations of B molecules ($\Delta\nu_B$)	change in ν_{OH}	disappearance of ν_{OH}, appearance of ν_{BH^+} and $\delta^{as}_{BH^+}$	change in ν_{HX}
Most exact method of determining the strength of the centres	from the change in frequency of the characteristic vibrations ($\Delta\nu_B = \nu_B - \nu_B^{gas}$) expressed in a scale of heat of adsorption; $Q = 10.5 + 0.5\nu_{CO}$ for CO	from ν_{OH}, in a proton affinity scale; $PA^{OH} = 1390 - \frac{\lg(\Delta\nu_{OH}/\Delta\nu_{OH}^{SiOH})}{0.00226}$	from the heats of formation of ion pairs	from $\Delta\nu_{HX}$ in the PA scale; $PA^{B_S} = \frac{3.54 + \lg\Delta\nu}{0.0057}$ CD for $CDCl_3$
Method of calculating the concentration of the centres	from the intensity of the characteristic bands of the B molecules	from the intensity of the ν_{OH} band	from the intensity of the most characteristic bands of the spectrum	from the intensity of the ν_{HX} band
Required physicochemical properties of the probes	to characterise the centres fully we must cover a range of dipole moment (μ) and of functional groups giving a $\Delta\nu_B$ shift on complex formation greater than the line width of ν_B (usually CN, CO)	absence of OH groups	the ν_{BH^+} band should not overlap the ν_B, H-complex, or M^{n+}:B bands	the ν_{HX} band should not overlap the ν_{OH} or ν_{CH} bands
Most widely used probes	acetone, pyridine, ammonia, acetonitrile, benzonitrile, carbon monoxide	nitromethane, acetonitrile, benzonitrile, acetone, dioxan, diethyl ether, tetrahydrofuran, pyridine and substituted pyridines, aniline, amines	ammonia, pyridine, and its derivatives	deuteriated chloroform

* A change in the number and position of the absorption bands of the B molecules may be observed under these conditions.

reliably identified and differentiated; 2) the strength of the individual centres should be determinable numerically, on a defined scale; 3) the concentration of each type of surface centre should be independently determinable.

These requirements are most easily met by spectroscopic methods, in particular the i.r. spectroscopy of adsorbed molecules. Unfortunately, very few studies of acidic or basic centres are mentioned in recent reviews[2,8,9] of advances in i.r. spectroscopy. The aim of the present review is to fill this gap.

The most basic application of i.r. spectroscopy to the study of the acid–base properties of surfaces is the spectral probe method, in which the properties of adsorption centres are characterised through the absorption spectra of molecules adsorbed on them and through the change in intensity of the bands associated with functional groups of the surface. The main features of this method as applied to the study of different types of centre are outlined in Table 1, which shows the types of complex formed by probe molecules with OH, L, and B_S centres, defines the vibrations used to measure the strength and number of surface centres, lists the most important physicochemical and spectral properties of the probe molecule, and names the probes most widely used as bases (B) to study acidic centres and as acids (HX) to study basic centres. Table 1 can be used as a starting point in the search for new probes and in the selection of a suitable method of characterising the acid–base properties of a particular catalyst. Let us examine each method in turn.

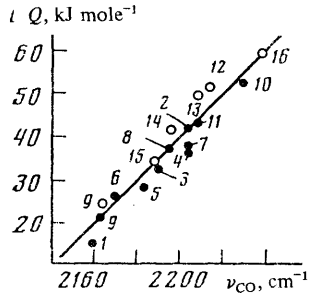


Figure 1. Correlation between νCO and the heat of adsorption Q of carbon monoxide on different surfaces: *1*) MgO, *2*) and *3*) γ-Al_2O_3, *4*) and *5*) ZrO_2, *6*) Ga_2O_3, *7*) and *8*) BeO, *9*) NaY, *10*) H-erionite, *11*) TiO_2, *12*) ZnY, *13*) MnY, *15*) CaY, *16*) Al_2O_3. The data *1–11* are taken from Ref.14, *9*, *12*, and *15* from Ref.15, *16* from Ref.16. The filled circles denote i.r. spectral data, the open circles calorimetric data. Points *2* and *3*, *4* and *5*, and *7* and *8* are for different complexes of the probe on the same adsorbent.

II. STUDY OF APROTIC CENTRES

1. Physicochemical Foundations of the Method

The strength of an aprotic centre is most correctly characterised by the free energy (ΔG) and the enthalpy (ΔH) of its interaction with a base[10]:

$$L + B \rightarrow L{:}B \qquad (I)$$

Since both protonic and aprotic centres are present simultaneously on the surface those quantities cannot be determined directly from measurements of the heat of reaction, as most probes react with both L and OH centres. It has therefore been suggested[11] that the strength of the L centres could be conveniently characterised by the quantity $\Delta\nu_B = \nu_B^{ads} - \nu_B^{gas}$, where ν_B^{ads} is the shifted absorption band in the spectrum of the adsorbed probe, on the assumption that $\Delta\nu_B$ is proportional to the extent of interaction of L and B in the donor–acceptor (D–A) complex. The main problem in using this assumption is that the formation of a D–A complex usually causes a rearrangement of both the electronic and the geometric structure of the probe molecule, both of which are reflected by the change in ν_B in the vibrational spectrum.

In specific cases this assumption has been confirmed both experimentally[12] and theoretically[13]. We have reported[14] an i.r. spectroscopic study of the correlation between the heat of adsorption of carbon monoxide and $\Delta\nu_{CO}$ on the metal cations for a series of silicate and oxide systems. The correlation (Fig.1) for the transition metal cations, and also Zr^{4+}, Zn^{2+}, and Mn^{2+}, can be described analytically as

$$Q, \text{ kJ mole}^{-1} = 10.5 + 0.5\,\Delta\nu_{CO} \qquad (1)$$

where $\Delta\nu_{CO} = \nu_{CO}^{ads} - 2143$ (cm^{-1}). By using this equation the strength of the aprotic centres can be determined (on the heat of adsorption scale) from the measured shift $\Delta\nu CO$ of the adsorbed carbon monoxide molecule.

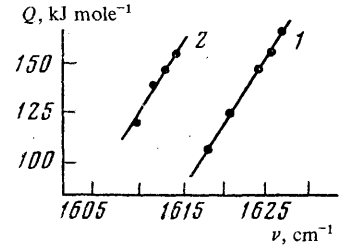


Figure 2. Relationship between the isosteric heat of adsorption of pyridine and the ν_{8a} frequency on aluminium oxide and zeolite (*1*) and on zirconium oxide (*2*).[17]

We have studied[17] the correlation between the heat of adsorption of pyridine on aluminium and zirconium oxides and the frequency of the absorption band for the pyridine ring which is most sensitive to co-ordination[18] ($\nu_{8a}^0 = 1580$ cm^{-1}). For the complexes with aprotic centres formed by the cations of one metal we found that ν_{8a} varies linearly with the heat of adsorption. For example, for Al^{III} (curve *1* of Fig.2) the correlation is

$$Q, \text{ kJ mole}^{-1} = 6.55 \cdot (\nu_{8a} - 1580) - 86 \qquad (2a)$$

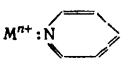
whereas for the Zr^{4+} cation the correlation (curve *2* of Fig.2) is

$$Q, \text{ kJ mole}^{-1} = 7 \cdot (\nu_{8a} - 1580) - 26 \qquad (2b)$$

This means that in the case of pyridine the position of the ν_{8a} band in the D–A complex with an aprotic centre can be used as a measure of the strength of the centre if only one metal cation is present.

Thus it is essential to establish the correlation between $\Delta\nu_B$ and Q before using a compound as a spectroscopic probe to measure the strength of aprotic centres.

Table 2. Properties of probe molecules used to study surface Lewis-acid centres.

No.	Probe	μ, D	Interaction with Lewis-acid centres: Complex	Interaction with Lewis-acid centres: Frequency used to measure strength of centres	Interaction with Lewis-acid centres: Frequency used to measure concentration of centres	Possible complications from interaction with Brønsted centres	Remarks
1	Acetone	2.82	$M^{n+}:O=C(CH_3)_2$	ν_{CO} (ν^0_{CO} = 1720 cm^{-1}) decreases; $\Delta\nu \leq 150$ cm^{-1}	no data	H-complex is formed; ν_{CO} decreases by 20–40 cm^{-1}	easily oxidised
2	Ammonia	1.48	$M^{n+}:NH_3$	δNH_3 ($\delta^0_{NH_3}$ = 968 cm^{-1}) increases; $\Delta\nu \leq 300$ cm^{-1}	from δ_{NH} intensity, δ^0 = 1620–1640 cm^{-1}	H-complex is formed, with $\delta NH_3 \cong$ 1620–1640 cm^{-1}	unsuitable because of partial amination of surface
3	Pyridine	2.20	M^{n+}: 	$\nu_{CC(N)} = \nu_{8a}$ (ν^0_{8a} = 1583 cm^{-1}); increases, $\Delta\nu \leq 40$ cm^{-1}	from intensity of $\nu_{CC(N)}$ = 1583 cm^{-1}, $\nu_{CC(N)}$ = 1445 cm^{-1}	H-complex is formed, $\nu_{CC(N)}$ = 1445–1450 cm^{-1}; ion pair gives overlapping bands, $\nu_{CC(N)}$ = 1610–1640 cm^{-1}	correlation between $\Delta\nu_B$ and ΔH for complexes with same cation
				$\nu_{CC(N)}$ ($\nu^0_{CC(N)}$ = 1445 cm^{-1}) increases, $\Delta\nu \leq 20$ cm^{-1}			
4	Acetonitrile	3.94	$M^{n+}:N\equiv C-CH_3$	ν_{CN} (ν^0_{CN} = 2275 cm^{-1}) increases, $\Delta\nu \leq 60$ cm^{-1}	from intensity of ν_{CN}	H-complex formed, $\Delta\nu_{CN} \cong$ 5–10 cm^{-1}	deutero-acetonitrile is better, because the ν_{CN} band shows Fermi resonance with $\nu_{CC} + \delta CH_3$ = 2290 cm^{-1}
5	Benzonitrile	4.39	$M^{n+}:N\equiv C-Ph$	ν_{CN} (ν^0_{CN} = 2229 cm^{-1}) increases, $\Delta\nu \leq 65$ cm^{-1}	from intensity of ν_{CN}	H-complex formed, $\Delta\nu_{CN} \cong$ 5–10 cm^{-1}	convenient because of high intensity of ν_{CN}
6	Carbon	0.1	$M^{n+}:C\equiv O$	ν_{CO} (ν^0_{CO} = 2143 cm^{-1}) increases, $\Delta\nu \leq 100$ cm^{-1}	from intensity of ν_{CO}	H-complex formed, $\Delta\nu_{CO} \cong$ 30 cm^{-1}	very unstable complexes; low-temperature adsorption essential

* Allowing for Fermi resonance.

Though the series of aprotic acids (in order of strength) is not usually the same for solutions of different bases, we can define two classes of bases which give similar aprotic acids: the "hard" bases, usually with a large dipole moment (μ), and the "soft" bases, which have no dipole moment but are easily polarised[19]. It is reasonable to expect a similar behaviour when the bases form surface complexes. Some properties of soft and of hard bases which can be used to measure the strength of surface centres are listed in Table 2.

It is clear from published data[14,16,20,21,22] that even on a single catalyst the $\Delta\nu_{CO}$ values for a metal cation in different co-ordinations can be very different: for example, for Al^{3+} and ν_{CO} frequency varies from 2190 to 2240 cm^{-1}. Even in simple oxides several types of complex between CO and the L centres are observed[14,16]. Therefore this probe molecule, being a soft base, can be used to identify the different states of the cation of a given metal in different co-ordinations.

A different situation is observed when "hard" bases are used as probes. It is found[23] that the ν_B frequencies for pyridine, benzonitrile, and acetonitrile (the probes most often used to study electron-acceptor centres) are almost constant for the cation of a given metal in different catalysts (oxides, amorphous or crystalline alumina–silicas, phosphates, germanates, molybdates, and antimonates). Therefore the position of the ν_B band is determined by the nature of the cation. The quantity γ_r^{n+} can be used to characterise the cation: it is defined as the ratio I^{n+}/r, where I^{n+} is the appropriate value of the ionisation potential of the metal cation (in eV) and r is its orbital radius (in Å).[24] Physically the quantity γ_r^{n+} is closely related to e/r, but it allows for differences between metal cations formally in the same state of oxidation[24]. Fig.3 shows a plot of ν_{CN} in the spectrum of benzonitrile adsorbed on different substances[23,25] against the γ_r^{n+} value of the appropriate metal cation. The plot is fitted by the equation

$$\nu_{CN} = 2228\,(\pm 3) + 5{,}18\,(\pm 0{,}37)\,(\gamma_r^{n+})^{1/2} \qquad (3)$$

with a correlation coefficient $|R| = 0.97$ and a standard deviation of the ν_{CN} values of 5 cm^{-1}.

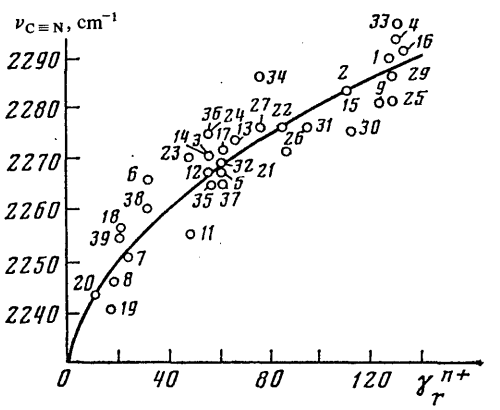


Figure 3. Dependence of ν_{CN} for benzonitrile adsorbed on catalysts upon γ_r^{n+}: *1*) Al_2O_3–SiO_2, *2*) Ga_2O_3–SiO_2, *3*) ZrO_2–SiO_2, *4*) BeO–SiO_2, *5*) MgO–SiO_2, *6*) Y_2O_3–SiO_2, *7*) La_2O_3–SiO_2, *8*) NaY, *9*) HNaY, *11*) CoNaY, *12*) NiNaY, *13*) CuNaY, *14*) ZrO_2–GeO_2, *15*) Ga_2O_3–GeO_2, *16*) BeO–GeO_2, *17*) MgO–P_2O_5, *18*) CaO–P_2O_5, *19*) SrO–P_2O_5, *20*) BaO–P_2O_5, *21*) Fe_2O_3–P_2O_5, *22*) Fe_2O_3–MoO_3, *23*) CoO–MoO_3, *24*) NiO–MoO_3, *25*) Al_2O_3–Sb_2O_5, *26*) Fe_2O_3–Sb_2O_5, *27*) Ga_2O_3–Sb_2O_5, *29*) γ-Al_2O_3, *30*) Ga_2O_3, *31*) TiO_2, *32*) ZnO, *33*) BeO, *34*) Cr_2O_3, *35*) ZrO_2, *36*) NiO, *37*) MgO, *38*) ThO_2, *39*) CaO. *1*)–*29*) from Ref.23, *30*)–*39*) from Ref.25.

Eqn.(3) can be used to study electron-acceptor centres in complex oxide systems containing various additives. Let us examine, for example, iron antimonate[26]. Taking tabulated values of γ_r^{n+} for all the cations which may be present on the surface (Fe^{3+}, Sb^{3+}, Sb^{5+}), and calculating the ν_{CN} frequencies by Eqn.(3), we obtain the ν_{calc} values 2276, 2255, and 2291 cm^{-1} respectively. By comparing them with

ν_{exper} (2270 and 2247 cm^{-1}) we conclude that the aprotic centres most likely to be present in iron antimonate are the iron and the antimony(III) cations.

No satisfactory explanation has yet been proposed for the low sensitivity of the position of the ν_B band to changes in the electronic state of the metal cation coupled with a high sensitivity to the nature of the metal cation. Some tentative suggestions appear in Ref.23.

It follows that in order to characterise fully an electron-acceptor centre on a catalyst surface we must use at least one hard and one soft base as probes (see Tables 1 and 2). The hard probe identifies the metal cations which form electron-acceptor centres, and the soft probe detects differences in the properties of a given cation in different environments.

2. Determination of the Concentration of L Centres

The surface concentrations are measured by assuming that the Beer–Lambert law is applicable to the bonds of adsorbed molecules. The most convenient form of this law is

$$A = 10^{-3} \cdot A_0 c_s \rho \qquad (4)$$

where A is the observed integral absorption for the analytical band in cm^{-1} (an analogous expression can be written for the optical density D), A_0 is the integral intensity of the band for a concentration of 10^{-6} mole $litre^{-1}$, c_S is the concentration of surface centres (expressed as μmole g^{-1} of catalysts), and ρ is the amount of catalyst (in mg) exposed to 1 cm^2 of the cross-section of the light beam. The product $10^{-3} c_S \rho$ gives the number of μmole of adsorbate in 1 cm^2 of the cross-section of the light beam. To find c_S we need to know A_0 (or the extinction coefficient ε if the optical density D is used). When overlapping bands (due to different forms of adsorption) are present, as is often the case since surface centres tend to be inhomogeneous, the complex band must be resolved into its individual components.

Unfortunately the A_0 coefficient has been obtained only in a few cases. The values of A_0 for the complexes of CO with Zn^{2+} are given in Ref.22. A_0 values for carbon monoxide forming D–A complpxes with a series of transition metal cations have also been reported[27]. A_0 has also been determined for the complexes of pyridine with aluminium cations[28], and the A_0 values have been studied[29] for some absorption bands of pyridine and of 2,6-dimethylpyridine interacting with NaY zeolite.

Thus it is clear that the absolute values of c_S for L centres can be measured only in a few cases from the i.r. absorption spectra of adsorbed molecules, and that the determination of the A_0 coefficients for the absorption bands of a wide range of individual probe molecules has become an urgent problem.

In studies of a series of chemically similar catalysts we can detect changes in the concentration of surface centres without knowing the A_0 coefficient. If the Beer-Lambert law is obeyed the parameter A for any of the ν_B bands is proportional to the concentration of the corresponding centres, and therefore the changes in A (normalised for $\rho = 1$) reflect the changes in the concentration of surface centres. This approach has been used[30–32] to reveal the nature of the catalytically active centres in a number of zeolites and zeolite-containing catalysts.

It is important in this connection to define the conditions under which the Beer–Lambert law is obeyed. Published data[14,22,28,33–35] suggest that this law is not infringed if two conditions are satisfied simultaneously: 1) the position of ν_B is unaffected by changes in surface coverage, and 2) the coverage of the adsorbent surface by adsorbate molecules is much less than a monolayer. Recommended values of ν_B for the most commonly used probes are given in Table 2. We should also bear in mind that the concentration of adsorption centres is not always equal to the number of adsorbed molecules per unit surface area. Adsorption should be carried out under conditions which ensure 100% filling of the centres of interest (or, at least, the same fractional filling in different experiments).

Thus the surface concentration of aprotic centres can be determined quantitatively by i.r. spectroscopy at three distinct levels of complexity and reliability. The first is suitable for qualitative studies of the changes in concentration of the centres in series of closely similar catalysts. We merely measure the change in intensity of the ν_B band, referred to 1 g of the catalyst. These experiments can be carried out in the simplest apparatus, using standard conditions for the adsorption of the probe. The second level of complexity is the determination of the concentration of surface centres by using published values of A_0. In this case the adsorption of the probe must be controlled to give almost 100% filling of the centres: this can be achieved by using a high relative pressure of adsorbate vapour or a low adsorption temperature. Usually under these conditions the probe is adsorbed in more than one form, and therefore the combined overlapping absorption bands must be resolved into the individual components before determining c_S. The third level of measurement complexity is reached when the concentration of acid centres on the surface has to be determined with a probe for which the A_0 value is not known. In this type of work the adsorption apparatus and the i.r. cell must be designed to allow simultaneous determinations of the adsorption and spectral measurements over a wide range of temperature and pressure. With this exception the third level does not differ from the second: it is potentially the most useful of the three levels, and it is attracting increasing interest.

We must now examine in detail the experimental methods of determining A_0. In order to find A_0 we need to know the surface concentration of the probe molecules, corresponding to the observed intensity of the experimental ν_B band. Some workers[36–40] have evaluated surface concentrations in parallel adsorption measurements, but as Little[41] has pointed out this can lead to serious errors because of the difficulty of reproducing exactly the conditions in adsorption experiments and i.r. spectral experiments.

An attempt[35] to make these conditions identical as far as possible by using pressed samples and by heating the adsorption sample to 50 °C (to simulate the heating of the spectral sample by i.r. radiation) was inconclusive, since no evidence was obtained that exactly equal amounts of pyridine were adsorbed on the same type of centre in the two pressed samples.

Undoubtedly the best approach is to determine the surface concentration of B centres and the parameter A for the ν_B band on a single sample in the same experiment. Two basic methods are available: the volumetric and the gravimetric method.

Volumetric method. The volumetric method often takes the form of a titration. Known amounts of adsorbate are added successively to the cell, and the spectrum is recorded after each addition. This approach has been used[28] to measure A_0 for the ν_B bands of pyridine and piperidine sorbed on decationated Y zeolite, aluminium oxide, and amorphous alumina–silica.

The use of the volumetric method is complicated in some cases by the adsorption of the probe molecules on the unheated parts of the cell. Quantitative corrections for the

adsorption on the cell walls are difficult to apply. In order to eliminate the effect provisions for heating the whole cell must be made, and the adsorption must be carried out at pressures well below the saturated vapour pressure of the probe at the temperature of the cell wall. The volumetric method can be used, without a correction for the adsorption on the cell wall and without heating the cell, to study the adsorption of carbon monoxide[14], ammonia ($T_b = 239.6$ K), acetone ($T_b = 329.6$ K), and acetonitrile ($T_b = 353.2$ K) at pressures up to 10 mmHg. With pyridine ($T_b = 388.4$ K) the adsorption on the cell wall at 300 K is negligible at pressures below 10^{-1} mmHg. For benzonitrile ($T_b = 463.8$ K) the volumetric method is probably inapplicable, since its vapour pressure at 300 K is 0.1 mmHg.

Gravimetric method. The gravimetric method consists in measuring the weight of the sample before and after admitting the adsorbate into the cell. Since the pressed samples used to measure the i.r. spectra are small, and the average concentration of acidic centres is also small, the precision of the measurement of sample weight should be at least 10^{-7} N.[42-44] As a result, a fairly complicated cell design is needed for simultaneous gravimetric and i.r. spectral measurements. For a detailed description of different types of these cells the reader is referred to recent monographs[18,41]. The apparatus must also include a system for introducing the adsorbate and means for measuring pressure.

The gravimetric method of measuring the amount of B molecules on the surface seems to be preferable to the volumetric method in two circumstances:

1) with weakly adsorbed gases (for example, alkenes[42]), when the precision of the volumetric method is inadequate. A comparison of the results obtained by both methods for the adsorption of unsaturated hydrocarbons is given in Refs.42 and 45.

2) for the adsorption of high-boiling probe substances, when the adsorption of B molecules on the cold wall of the cell is significant.

The gravimetric method should be chosen when pyridine is used as the adsorbate[35] (and probably also benzonitrile). A more detailed description of the properties of the probes listed in Table 2 and of their special features in use can be found in Refs.3, 11, 14–16, 18, 23, 24, 30–32, 42, and 46–54.

Evidently these difficulties in the determination of the surface concentrations of adsorbed substances from their i.r. spectra are not confined to the aprotic centres. Studies of protonic or basic centres present similar problems, which can be overcome in similar ways. Therefore we shall limit our discussion of the determination of the concentration of the latter types of centre to a few specific cases.

III. STUDY OF PROTONIC ACID CENTRES

1. The Concepts of "Acid Strength" and "Acidity", and their Measurement Units

The theory of acids and bases is most fully developed for aqueous solutions[55], but it includes a group of concepts which can be used in the qualitative and quantitative description of the properties of any solution. Three of these concepts are especially relevant to the present discussion: the acid (or base) strength, the acidity of the solution, and the solvation effect. According to Hammett[56] the acid or base strength denotes the extent to which the acid is converted into an anion (or the base into its conjugated acid) under standard conditions. These degrees of conversion are characterised by the appropriate equilibrium constants, or in pK_a units.

Thus the "acid strength" is a thermodynamic quantity which describes the properties of substances in relation to a chosen standard medium. The second concept ("acidity of the solution") describes the tendency of the solution as a whole to donate a proton to a base. This tendency increases with the concentration of the acid. In dilute aqueous solutions it is measured by the pH, or by the more universal acidity function H_0 (which is less dependent on the solvent)[56]. If the tendency of the acid to transfer a proton to the base is characterised by the protolytic base indicator equilibrium

$$HInd^+ \rightleftarrows Ind + H^+ \qquad (II)$$

for which we can write

$$K_a = \frac{a_{H^+} a_{Ind}}{a_{HInd^+}} \quad \text{or} \quad pK_a^{Ind} = -\lg \frac{a_{H^+} f_{Ind}}{f_{HInd^+}} + \lg \frac{[HInd^+]}{[Ind]}$$

where a is the activity and f the activity coefficient in the given medium, the acidity function is given by the expression

$$H_0 = pK_a^{Ind} - \lg \frac{[HInd^+]}{[Ind]} \qquad (5)$$

The quantity $H_0 = -\lg a_{H^+} f_{Ind}/f_{HInd^+}$ is a measure of the acidity of the medium. It is important to note that the scale of H_0 characterises the acidity of the solution but not the acid strength, since it depends on the concentration of the acid. It is applicable when: 1) the protonation of the base [described by Eqn.(II)] has reached equilibrium, and 2) the properties of the uncharged Ind molecules allow the ratio f_{Ind}/f_{HInd^+} in the given medium to be constant for any indicator. For equal concentrations of the protonated and of the initial base the H_0 value is equal to the pK_a of the indicator.

The indicator method was later extended by Walling[4] to solid acids by postulating that the ability of a surface to convert a base into a protonated acid can be characterised in the H_0 scale. The surface is treated as a medium with a high dielectric constant, and H_0 as a measure of the acid strength (determined from the pK_a value for the weakest of the protonated base indicators adsorbed from non-polar solvents). The second term of Eqn.(5) was ignored. Thus a confusion in the use of the "acid strength" concept arose at that early stage in the development of the study of the acidity of solids.

The need to quantify the strength of solid acids arose during the development of heterogeneous acid–base catalysis. However, in catalytic reactions the base is in the gas phase, and therefore it is more correct to examine the tendency of the catalyst surface to protonate the base after it has been adsorbed from the gas phase. In other words, whereas the acid strength in an aqueous solution is characterised by the equilibrium constant for the dissociation

$$AH \overset{K_a}{\rightleftarrows} A^- + H^+ \qquad (III)$$

no such dissociation takes place on the surface, and the protonation of the base cannot be described by the simple equation (II).

The mechanism of the interaction of a molecule of a gaseous base B with a protonic acid centre on a solid surface can be described[57] by the scheme

$$\underset{A}{|-OH} + B^{gas} \rightarrow \underset{H\text{-complex}}{|-O-H \ldots B} \rightarrow \underset{IP}{|-O^- \ldots {}^+HB} \qquad (IV)$$

where A is the initial state of the system, H-complex is a complex in which B is hydrogen-bonded to an acidic OH group, and IP is an ion pair. A similar mechanism applies to the interaction between an acid and a base in non-polar

solvents[58]. According to this scheme the tendency of protonic acid centres to interact with the base B can be determined by studying the reaction between A and the H-complex or between A and IP. In the following sub-sections we shall examine both these approaches, which have been called respectively the "hydrogen bond method" and the "ion pair method".

Recent work[59–74] has established that the strength of a Brønsted acid or base in the gas phase is more correctly defined through the "proton affinity" (PA). In the case of acids the PA is determined by the enthalpy (ΔH) of the reaction

$$AH \rightarrow A^- + H^+ \qquad (V)$$

and the PA of bases by the enthalpy of the reaction

$$HB^+ \rightarrow H^+ + B \qquad (VI)$$

Both reactions are assumed to take place in the gas phase.

Table 3. Probes used to study Brønsted acid centres.

No.	Probe	pK_a [75—78]	PA, kJ mole^{-1} (Ref. 59,60, 68–74)	$\Delta\nu_{OH}$, cm^{-1} **		Criterion for the formation of an ion pair (IP)
				SiO_2	HNaY	
1	Argon	—	377	8	34	not formed *
2	Oxygen	—	423	12	37	»
3	Krypton	—	435	16	60	»
4	Xenon	—	477	19	—	»
5	Nitrogen	—	477	24	91	»
6	Cyclohexane	—	586	45	—	»
7	Carbon monoxide	—	598	90	250	»
8	Chloromethane	—	670	110	—	»
9	Nitromethane	11.93	753	160	550	»
10	Acetaldehyde	—	774	290	—	»
11	Ethyl methyl ketone	−7.2	774	330	—	»
12	Dioxan	−3.22	799	390	1000	»
13	Acetone	−7.2	816	340	900	»
14	Tetrahydrofuran	−2.02	820	470	1000	»
15	Diethyl ether	−2.42	824	460	1000	»
16	Acetophenone	−6.15	833	320	—	»
17	Methyl acetate	—	816	270	—	»
18	Dimethylsulphoxide	0	870	550	1050	»
19	Benzonitrile	−10.43	—	300	750	»
20	Acetonitrile	−10.13	783	300	750	»
21	Ammonia	9.25	846	750	—	$\delta_{NH_4^+}$ = 1400—1450 cm^{-1}
22	Tripropylamine	11.0	940	990	—	—
23	Aniline	4.81	874	500	—	—
24	Methylimidazole	6.95	—	830	—	—
25	Diethylamine	10.7	929	930	—	—
26	Trimethylamine	9.67	929	990	—	—
27	Piperidine	11.22	933	980	—	—
28	Triethylamine	11.02	958	990	—	—
29	Perchloropyridine	−8	—	270	850	ν_{NH} = 3250 cm^{-1}
30	2,5-Dibromopyridine	−3	—	450	1000	$\nu_{CC(N)}$ = 1520 cm^{-1}
31	2-Bromopyridine	0.8	891	580	1150	$\nu_{CC(N)}$ = 1530 cm^{-1}
32	3-Chloropyridine	3.6	891	630	—	—
33	Pyridine	5.21	912	750	1250	$\nu_{CC(N)}$ = 1540 cm^{-1}
34	2-Methoxypyridine	3.28	912	550	—	—
35	2-Methylpyridine	5.97	925	750	—	—
36	Hydrogen sulphide	—	714	150	—	—
37	Dimethyl sulphide	−5.25	824	370	—	—

Notes. The bases in this Table are classified into groups as follows: Nos.1–8 do not show basic properties in aqueous solutions, Nos.9–18 are oxygen-containing bases, Nos.19–28 are nitrogen-containing bases, Nos.29–35 are pyridine and its derivatives, Nos.36 and 37 are sulphur-containing bases. The dash denotes the absence of suitable data. Probes No.1–5 were adsorbed at low temperature, No.13 is difficult to use (readily oxidised), No.21 tends to aminate the surface. With probes No.21–28 the donor–acceptor complexes are difficult to distinguish from protonated molecules, Nos.29–31 have a low vapour pressure.

* Ion pairs are not formed on protonic centres with PA > 1200 kJ mole^{-1}.

** Data taken from Refs.41, 91–93, 96–98.

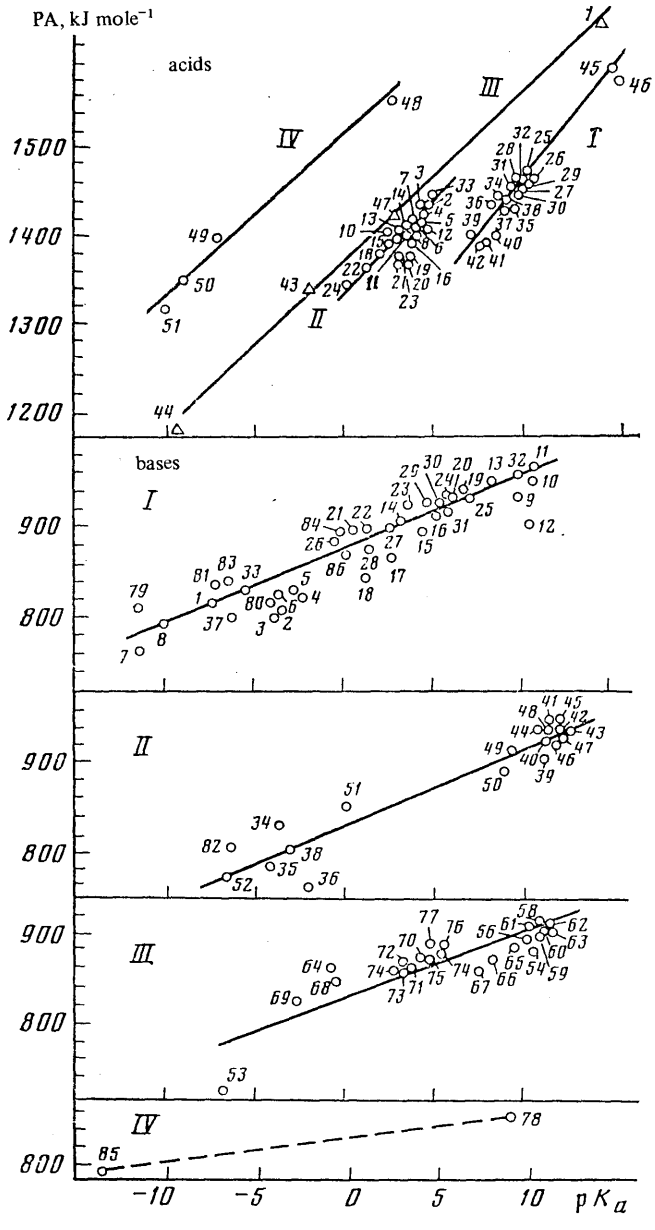


Figure 4. Correlation between PA and pK_a for different types of acid and base. Bases: (*I*) no protons on the proton-acceptor atom, (*II*) one proton, (*III*) two protons, (*IV*) three protons. Acids: (*I*) alcohols and phenols, (*II*) carboxylic acids, (*III*) inorganic oxygen-containing acids, (*IV*) hydrogen halide acids. Bases: *1*) acetone, *2*) dioxan, *3*) dimethyl ether, *4*) tetrahydrofuran, *5*) tetrahydropyran, *6*) diethyl ether, *7*) nitromethane, *8*) acetonitrile, *9*) trimethylamine, *10*) triethylamine, *11*) tri-n-propylamine, *12*) methylcyclobutylamine, *13*) triallylamine, *14*) tripropylamine, *15*) 2,2,2-trifluoroethylamine, *16*) pyridine, *17*) 4-trifluoromethylpyridine, *18*) 4-nitropyridine, *19*) 4-methoxypyridine, *20*) 4-methylpyridine, *21*) 2-chloropyridine, *22*) 2-bromopyridine, *23*) 2-methoxypyridine, *24*) 2-methylpyridine, *25*) 2-aminopyridine, *26*) 2-fluoropyridine, *27*) 3-chloropyridine, *28*) 3-cyanopyridine, *29*) 3-methoxypyridine, *30*) 3-methylpyridine, *31*) 3-aminopyridine, *32*) 4-aminopyridine, *33*) dimethyl sulphide, *34*) t-butanol, *35*) n-butanol, *36*) methanol, *37*) acetic acid, *38*) isopropanol,

39) dimethylamine, *40*) diethylamine, *41*) di-n-propylamine, *42*) di-isopropylamine, *43*) di-n-butylamine, *44*) di-isobutylamine, *45*) di-s-butylamine, *46*) cyclopropylamine, *47*) cyclobutylamine, *48*) cyclopentylamine, *49*) diallylamine, *50*) dipropylamine, *51*) pyrrole, *52*) methyl sulphide, *53*) water, *54*) methylamine, *55*) ethylamine, *56*) n-propylamine, *57*) isopropylamine, *58*) n-butylamine, *59*) isobutylamine, *60*) s-butylamine, *61*) t-butylamine, *62*) n-pentylamine, *63*) t-ethylamine, *64*) hydrazine, *65*) allylamine, *66*) propylamine, *67*) 2-isocyanoethylamine, *68*) acetamide, *69*) formamide, *70*) aniline, *71*) 3-fluoroaniline, *72*) 3-chloroaniline, *73*) 4-chloroaniline, *74*) 3-methylaniline, *75*) 4-methylaniline, *76*) 3-methoxyaniline, *77*) 4-methoxyaniline, *78*) ammonia, *79*) benzonitrile, *80*) ethyl methyl ether, *81*) benzaldehyde, *82*) phenol, *83*) methyl phenyl ether, *84*) *N,N*-dimethylacetamide, *85*) phosphine, *86*) dimethylsulphoxide. Acids: *1*) water, *2*) acetic acid, *3*) 4-methylbenzoic acid, *4*) 2-methoxybenzoic acid, *5*) 3-methylbenzoic acid, *6*) benzoic acid, *7*) 3-methoxybenzoic acid, *8*) 2-methoxybenzoic acid, *9*) 2-methylbenzoic acid, *10*) fluoroacetic acid, *11*) 2-fluorobenzoic acid, *12*) 3-fluorobenzoic acid, *13*) 2-chlorobenzoic acid, *14*) 4-fluorobenzoic acid, *15*) chloroacetic acid, *16*) 4-chlorobenzoic acid, *17*) 3-chlorobenzoic acid, *18*) 2-nitrobenzoic acid, *19*) 3-nitrobenzoic acid, *20*) 2-cyanobenzoic acid, *21*) 3-cyanobenzoic acid, *22*) dichloroacetic acid, *23*) 4-nitrobenzoic acid, *24*) trifluoroacetic acid, *25*) 4-methylphenol, *27*) 3-methylphenol, *28*) phenol, *29*) 2-methylphenol, *30*) 2-methoxyphenol, *31*) 3-methoxyphenol, *32*) 4-fluorophenol, *33*) propionic acid, *34*) 2-fluorophenol, *35*) 3-fluorophenol, *36*) 2-chlorophenol, *37*) 4-chlorophenol, *38*) 3-chlorophenol, *39*) 2-nitrophenol, *40*) 3-cyanophenol, *41*) 3-nitrophenol, *42*) 4-cyanophenol, *43*) nitric acid, *44*) perchloric acid, *45*) methanol, *46*) ethanol, *47*) nitrous acid, *48*) hydrogen fluoride, *49*) hydrogen chloride, *50*) hydrogen bromide, *51*) hydrogen iodide. PA data taken from Refs.59, 60, 64, 65, 67 for acids and from Refs.60, 61, 68–71, 73, 74 for bases. Data on pK_a taken from Refs.71, 75–78.

Experimentally the parameter PA is found by studying the equilibrium gas-phase proton transfer reactions between the acid and the acid residue or between the protonated and the free base. The enthalpy of the reaction is determined in relation to a chosen standard: in particular, ammonia, whose PA [determined directly by reaction (VI)] is 846 kJ mole^{-1}.[69]

Thus we can use the PA to characterise the interaction of acidic OH groups of the surface with B molecules in the gas phase, and the problem reduces to finding the functional relationship between any measurable property of the system which reflects the extent of proton transfer and the quantities PA_{AH} and PA_B. Under these conditions PA_B is always known (see Table 3). However, in many current publications the acid–base properties of surfaces are measured in pK_a units, and therefore the reported PA values have to be compared with the properties of the solute in water, i.e. on the pK_a scale. Data on pK_a and on the PA can be found in many recent papers[59–78] and in their References. In general, an increase in the PA of bases from 710 to 960 kJ mole^{-1} is accompanied by an increase in pK_a from (−14)–(−11) to (11)–(12). However, we should note that often the pK_a values differ by 10 or more units for substances with almost identical PA, and conversely for substances with similar values of pK_a the PA can differ by 100–120 kJ mole^{-1} (see Table 3).

Since the pK_a value is largely determined by the state of solvation of the ionised base, we can use specific features of the solvation as a basis for classification. In particular, we can expect bases with different numbers of protons on the acceptor atom (for example, primary, secondary, and tertiary amines) to form different numbers of hydrogen bonds with water molecules, and therefore to show differences in solvation energy for the same basicity.

This criterion is used in Fig.4 to establish correlations between pK_a and PA values for compounds containing equal numbers of protons. In each group of bases we find an obvious proportionality between the two parameters: the mean scatter is ~40 kJ mole^{-1} for the PA and ~3 units for pK_a. Even closer correlations between pK_a and the PA are found in series of isostructural bases[68,72].

We can also compare the PA and pK_a values of acids by classifying the acids into several groups (see Fig.4). Group I includes alcohols and phenols, group II the carboxylic acids, group III oxygen-containing inorganic acids and water, while group IV is reserved for hydrogen halides. It is clear from these results that only bases or acids of a given type can be arranged in order of strength (in the gas phase) from pK_a data obtained for these substances in aqueous solutions: to a first (and rough) approximation we can use the classification suggested above.

It has recently been suggested[79–81] that the thermodynamic characterisation of the proton-donor properties of catalysts should be supplemented by a kinetic criterion: the activation energy (E_a^H) for the transfer of the proton from the surface to the adsorbed molecule. A spectroscopic method of calculating E_a^H from measurements of ν_{OH} for the surface before and after adsorption was developed, using the specially established correlation between $\Delta\nu_{OH}$ and E_a^H.

Let us now examine in detail each of the above methods of quantifying the proton-donating properties of solid acids.

2. The Hydrogen Bond (HB) Method

a) *Physicochemical basis.* Attempts to characterise the strength of acids or bases through the properties of the H-complex [see reaction (IV)] raise two important questions: can the influence of the acid or base strength on the properties of the complex be revealed explicitly, and what is the relationship between the various properties of the H-complex and the thermodynamics of the proton transfer reaction.

Detailed and precise studies of the enthalpy of formation of the H-bond (ΔH_H) and of the change in frequency of the stretching vibrations ($\Delta\nu_{HX}$, $\Delta\nu_{OH}$) for the formation of the complex in non-aqueous solutions have been reported[82]. An unambiguous correlation between these quantities was demonstrated[82–86]. Since $\Delta\nu_{HX}$ is directly measurable from the i.r. spectra we shall use only this parameter to characterise the H-complexes.

The answer to the first question is given in a comparison [87–89] of various characteristics of the H-bond (including $\Delta\nu_{HX}$) with the properties of the acid or based involved, which led to the formulation of the following "factor rule": any parameter used to characterise the H-bond can be expressed as a product of a function describing the dependence of the stated parameter of the complex on the nature of the i-th acid (P_i) and a function describing its dependence on the nature of the j-th base (E_j). It was shown[86–88] that the ratio of $\Delta\nu_{HX}$ for any acid interacting with the base B to $\Delta\nu_{OH}$ for phenol (chosen as a standard) interacting with the same B is the same for all bases B, and depends only on the nature of HX: $\Delta\nu^B_{HX}/\Delta\nu^B_{OH(PhOH)} = \text{const} = P_i$. This suggests that the nature of the base has the same influence on

the $\Delta\nu_{HX}$ value of any acid: thus, if the P_i values are calculated for a series of acids the dependence of $\Delta\nu_{HX}$ on the nature of the acid can be obtained to the precision of a constant factor.

Furthermore, the ratio of the shift of the ν_{HX} frequency for different acids (HX) interacting with the same base B to the $\Delta\nu_{HX}$ value of the same acids interacting with another base chosen as a standard (for example, diethyl ether[87]) is also constant, and depends only on the nature of B and on the chosen standard: $\Delta\nu^{B}_{HX}/\Delta\nu^{(C_2H_5)_2O}_{HX} = \text{const} = E_j$. Thus the change of E_j for a series of B is a function describing the dependence of $\Delta\nu_{HX}$ on the nature of the base B to a precision determined by the choice of the standard B.

The full form of the function describing the effect on $\Delta\nu_{HX}$ for any acid of the interaction with the base B (taking PhOH and $(C_2H_5)_2O$ as standards) is

$$\Delta\nu_{HX} = C\left(\frac{\Delta\nu^{B}_{HX}}{\Delta\nu^{B}_{OH(PhOH)}}\right)\cdot\left(\frac{\Delta\nu^{B}_{HX}}{\Delta\nu^{(C_2H_5)_2O}_{HX}}\right)$$

where the constant C reflects the properties of the chosen standards. It is easily shown, by putting HX = PhOH, that $C = \Delta\nu^{(C_2H_5)_2O}_{OH(PhOH)}$. According to Iogansen[87], in this case $C = 282$ cm^{-1}, and therefore

$$\Delta\nu_{HX} = 282 P_i \cdot E_j \qquad (6)$$

By using Eqn.(6) we can establish the dependence of P_i on the relevant property of the acid (or the dependence of E_j on the property of the base) from experimental $\Delta\nu_{HX}$ data. Direct correlations between $\Delta\nu_{OH}$ in the H-complexes and the K_p (or $\lg K_p$) value (which characterises thermodynamically the proton transfer from the acid to the base) have not so far been reported. However, in a series of different B with the same OH acid or in a series of different acids with the same base the dependence of $\Delta\nu_{OH}$ on K_p is equivalent (to the precision of a constant term) to the dependence of $\Delta\nu_{OH}$ on pK_a^{base} or on pK_a^{acid}, since $-\lg K_p = pK_a^{acid} - pK_a^{base}$. This dependence of $\Delta\nu_{OD}$ (for deutero-methanol) on the pK_a values of various bases was first demonstrated by Hammett[90], and the dependence on pK_b by Gordi and co-workers (see Ref.82). According to Arnett[77] the dependence of $\Delta\nu_{OH}$ on pK_a^{base} can be described by the correlation equation

$$\Delta\nu_{OH}/\nu^{0}_{OH} = a + b\,pK_a^{base} \qquad (7)$$

This equation was proposed[91,92] for a strong H bond, formed on Aerosil, phosphates, or HNaY zeolite. For example, for Aerosil $a = 0.145 \pm 0.004$ and $b = 0.0096 \pm 0.0007$.

The dependence of $\Delta\nu_{OH}$ on the pK_a of adsorbed bases for Aerosil, with additional results from Ref.93, is shown in Fig.5. For bases of group I the dependence on pK_a^{base} can be fitted more accurately to the following equation than to a linear equation:

$$\Delta\nu_{OH} = 530(\pm 14)\cdot 10^{0.026(\pm 0.0015)pK_a^{base}} \qquad (8)$$

According to this equation we can calculate pK_a^{base} to a precision better than ± 1.4 pK_a units if $pK_a > -12$ and $\Delta\nu_{OH} > 150$ cm^{-1}. The standard deviation of the $\Delta\nu_{OH}$ values is less than ± 20 cm^{-1}.

The few available data on the adsorption of bases in groups II–IV gave $\Delta\nu_{OH}$ values lower by 100–200 cm^{-1} than the $\Delta\nu_{OH}$ values for group I bases at the same pK_a. This is consistent with the above conclusion that the correlation between pK_a and the characteristics of the acids (or bases) applies only within a single group of compounds.

Eqn.(8) is physically analogous to (6), since the factor 530 cm^{-1} is determined by the strength of the Aerosil (or other acid) and is proportional to P_i, and the term $10^{0.026}\,pK_a^{base}$ is proportional to E_j.

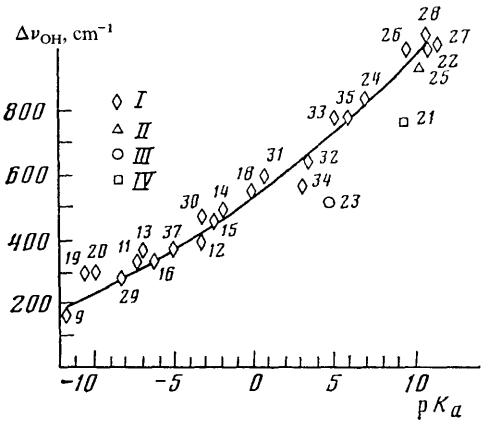


Figure 5. Dependence of $\Delta\nu_{OH}$ for the hydroxyl groups of Aerosil on the pK_a value of adsorbed bases: (*I*) bases from group I, (*II*) from group II, (*III*) from group III, (*IV*) ammonia. The numbering of the points corresponds to Table 3.

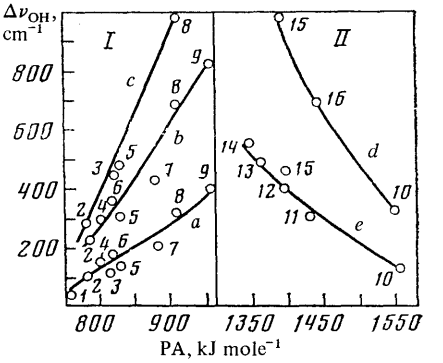


Figure 6. Dependence of $\Delta\nu_{OH}$ of the H-complexes on the PA of the bases (*I*) for t-butanol (*a*), 4-fluorophenol (*b*), and 4-nitrophenol (*c*), and on the PA of the acids (*II*) for acetone (*d*) and pyridine (*e*) in non-polar solvents. The numbering of the points denotes the base: *1*) nitromethane, *2*) acetonitrile, *3*) acetone, *4*) dioxan, *5*) diethyl ether, *6*) tetrahydrofuran, *7*) dimethylfluoramide, *8*) pyridine, *9*) triethylamine, *10*) t-butanol, *11*) acetic acid, *12*) chloroacetic acid, *13*) dichloroacetic acid, *14*) trifluoracetic acid, *15*) 4-nitrophenol, *16*) 4-fluorophenol. Data from Refs.88, 89, 99, and 100 were used.

Until recently there had been no attempt to find a correlation between $\Delta\nu_{OH}$ of the H-complex and the PA of acids or bases. Fig.6 shows the dependence of $\Delta\nu_{OH}$ for the H-complexes of some acids on the PA of bases (I), and for the complexes of some bases on the PA of acids (II) in non-polar

solvents, calculated from published data[89,90,99,100], with PA values taken from Refs.59–74. The dependences are practically linear, and the $\Delta\nu_{OH}$ values increase with the PA of the base, the slope of curves showing a marked increase as we change from the weak acid t-butanol (curve *a*) to the stronger acids 4-fluorophenol (curve *b*) and 4-nitrophenol (curve *c*). The $\Delta\nu_{OH}$ values decrease as the PA of the acid increases.

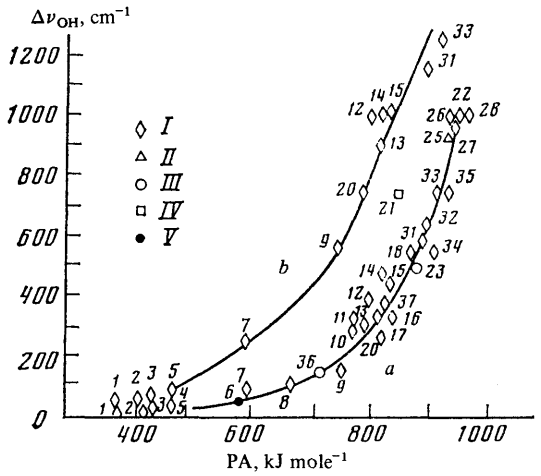


Figure 7. Dependence of $\Delta\nu_{OH}$ for H-complexes on the PA of adsorbed bases. Curve *a* refers to Aerosil, curve *b* to HNaY zeolite: (*I*) bases of group I, (*II*) group II, (*III*) group III, (*IV*) ammonia, (*V*) cyclohexane on Aerosil. The numbering of the points corresponds to Table 3.

We have observed[94] a correlation between $\Delta\nu_{OH}$ for the solid acids Aerosil and HNaY zeolite and the PA of adsorbed bases (Fig.7). For both acids, with $\Delta\nu_{OH} < 400$ cm^{-1} (weak hydrogen bond), the dependence is described by the equation

$$\Delta\nu_{OH} = \alpha' \cdot 10^{0.0036(\pm 0.0002)PA^{base}} \qquad (9)$$

where α' is a coefficient dependent on the properties of the acid. Changing from SiO_2 to a stronger acid (HNaY zeolite) causes α' to increase. Eqn.(9) also is similar to (6), with α' functionally related to P_i and the term $10^{0.0036}$ PAbase related to E_j. From Eqn.(9) we can find the PA of the base from the $\Delta\nu_{OH}$ values with a precision of ±20 kJ mole^{-1}.

For $\Delta\nu_{OH} > 400$ cm^{-1} we again find a clear correlation between $\Delta\nu_{OH}$ and PA^{base}. For bases with a PA between 850 and 960 kJ mole^{-1} the variation of $\Delta\nu_{OH}$ of Aerosil (say) with the PA of the base is accurately linear. With the exception of ammonia, all the bases (groups I–III) in Fig.7 accurately lie on the curves *a* or *b*. However, since the study of strong hydrogen bonds is often complicated by Fermi resonance[95], and since a base forming weak bonds can always be found for any solid acid (see Table 3), we shall confine our discussion to weak bonds.

Let us examine in detail the reported functional relationships between *b*, P_i (i.e. $\Delta\nu_{OH}$) and the pK_a or PA values of acids. The $\Delta\nu_{OH}$ values of silica gel, magnesium oxide, phosphoric acid, and B_2O_3 (on silica gel) have been measured[101] for the interaction with various aromatic compounds, CCl_4, and oxygen- or nitrogen-containing bases, and also $\Delta\nu_{OH(PhOH)}$ in a solution of CCl_4 in the presence of the same bases, in order to determine $\Delta\nu_{OH}^{sol}/\Delta\nu_{OH(PhOH)}$. At the same time the P_i values were obtained for non-aqueous solutions of the H-complexes of the acids and bases, and their dependence on the pK_a of the acids was analysed. Lastly, assuming that the same relationship is retained in heterophase systems, the pK_a values for the OH groups of Aerosil and magnesium oxide were obtained from the plot of P_i against pK_a and the $\Delta\nu_{OH}^{sol}/\Delta\nu_{OH(PhOH)}$ values. The results were +7 and +15.6 respectively.

A similar approach, with a wider range of P_i values for the acid solutions, has been used[102] to calculate the strength of the protonic centres in amorphous alumina-silicas. The pK_a value of the most acidic OH groups in this material was found to be $-(6 \pm 2)$.

It was also found[91,92] that in practice only the parameter *a* of Eqn.(7) depends on the strength of the acidic centre. This means that for a strong H bond the $\Delta\nu_{OH}$ value is determined (by an additive formula) by the strength of the acid and of the base. Since the relationship between *a* and pK_a^{acid} for a strong H bond in solution is not known, it may be described approximately by an expression analogous to Eqn.(7). Taking the value[101] of +7 for the pK_a of the OH groups in Aerosil we obtained[91,92] the following expression for calculating the strength of acidic surface OH groups on the pK_a scale to a precision of ±2.5 pK_a units:

$$\frac{\Delta\nu_{OH}}{\nu_{OH}^0} = 0.216 - 0.0096(\Delta pK_a) \qquad (10)$$

where $\Delta pK_a = pK_a^{acid} - pK_a^{base}$.

Table 4. Strength of the Brønsted acid centres, measured by different methods.

Method*	HNaY zeolite and alumina–silica	P_2O_5 on SiO_2 and on M_xO_y	SiO_2	MgO
Weak H-bond method, in pK_a units	−6	−0.4	+7	+15
Strong H-bond method, in pK_a units	−9	−5	+7	—
Weak H-bond method, on the PA scale (kJ mole^{-1})	1200	1300	1390	1560(±40)

* The methods are described in the text.

We have used Eqn.(10) to determined pK_a for the OH groups of HNaY zeolite and of metal phosphates (Table 4). We also studied[94] the correlation between the P_i values averaged over many bases in non-aqueous solutions and the PA for a series of acids (Fig.8). For oxygenated acids in $\lg P_i$—PA co-ordinates the dependence is accurately fitted by the straight line.

$$\lg P_i = \lg\beta + 0.00226(\pm 0.00016)\,PA^{acid} \qquad (11)$$

or, from the definition of P_i,

$$\Delta\nu_{OH}^{B} = \beta \cdot \Delta\nu_{OH(PhOH)}^{B} \cdot 10^{0.00226(\pm 0.00016)PA^{acid}} \qquad (12)$$

We note that the coefficient β, being the value of P_i at PA = 0, is independent of the strength of the base B. Eqn. (12) is valid for any B, but is assumes that $\Delta\nu_{OH}$ and

$\Delta\nu_{OH(PhOH)}$ have been measured for the interaction of the respective acids with the same base. By using this equation we can measure $\Delta\nu_{OH}$ and $\Delta\nu_{OH(PhOH)}$ in non-aqueous solutions and hence obtain the PA of the acid to a precision (defined as the standard deviation of P_i in Fig.8) better than ±25 kJ mole^{-1}. Eqn.(12) was assumed to be equally applicable to hetero-phase systems[94]. In other words, it was assumed that the points for which $P_i = \Delta\nu_{OH}^{sol}/\Delta\nu_{OH(PhOH)}$ could be included in the plot of Fig.8. By writing Eqn.(12) for SiOH(SiO_2) and for the solid acid OH†, and by dividing one expression by the other, we can eliminate the term $\beta.\Delta\nu_{OH(PhOH)}$, and solving for PA^{acid} we arrive at the following expression for PA:

$$PA^{OH} = PA^{SiOH} - \frac{1}{0.00226}\lg\frac{\Delta\nu_{OH}^{B}}{\Delta\nu_{OH(SiO_2)}^{B}} \qquad (13)$$

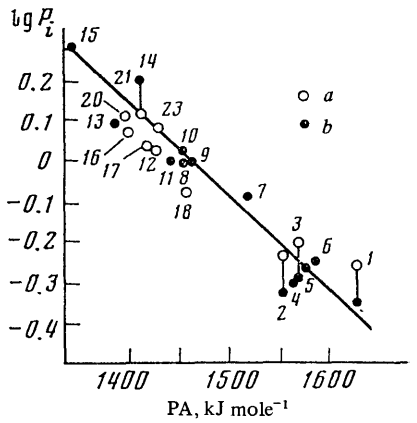


Figure 8. Correlation between lg P_i and the PA of the corresponding acids: *1*) water, *2*) t-butanol, *3*) isopropanol, *4*) n-propanol, *5*) ethanol, *6*) methanol, *7*) 2-trifluoroethanol, *8*) phenol, *9*) 4-methylphenol, *10*) 3-methylphenol, *11*) 4-fluorophenol, *12*) 4-chlorophenol, *13*) 4-nitrophenol, *14*) benzoic acid, *15*) trifluoroacetic acid, *16*) 4-nitrophenol, *17*) 3-chlorophenol, *18*) 4-methoxyphenol, *19*) acetic acid, *20*) chloroacetic acid, *21*) 3-methoxybenzoic acid. Points *a* from Ref.87, points *b* from Ref.102, PA values from Refs. 59, 66, and 73.

By changing to a new standard (Aerosil, with a PA of 1390 kJ mole^{-1} determined[102] according to Eqn.(11) (Fig.8) for $P_i = 1.2$)[102] we can not only avoid the need to calculate β and $\Delta\nu_{OH(PhOH)}$ when using different bases B, but also use a much wider range of bases. This is because phenol does not form stable H-complexes with some of the bases most commonly used to study solid acids, such as CO, probes No.1–6 in Table 3, etc.

To calculate the PA values of solid acids by Eqn.(13) we need to know $\Delta\nu_{OH}$ for the interaction of the base B on SiO_2 and on the solid acid under study. Like Eqn.(12), Eqn.(13) is valid only for oxygen acids. The precision of the determination of the PA by Eqn.(13) is ±25 kJ mole^{-1}. As the data in Fig.7 show, the choice of the base B cannot be arbitrary, since for $\Delta\nu_{OH} > 400$ cm^{-1} the logarithmic relationship between the PA and $\Delta\nu_{OH}$ ceases to apply. The study of the acidity of the OH groups on solids by using Eqn.(13) or the P_i–pK_a^{acid} correlation (which is limited in practice to the range of $\Delta\nu_{OH}$ values from 0 to 400 cm^{-1}) has been called the weak hydrogen bond method, whereas the study by Eqn.(10) is known as the strong hydrogen bond method.

By using Eqn.(13) we have shown[94] that the PA of the OH groups in decationated HNaY zeolite is 1200 kJ mole^{-1}. The difference in PA between Aerosil and zeolite is consistent with quantum-mechanical calculations[103].

Thus we can compare the different methods of determining the strength of acidic centres by listing their results for given systems (Table 4). On the whole all the methods yield similar sequences for the strength of the OH groups on different substances, but the last method [using Eqn.(13)] offers a higher relative precision in the determination of the parameter of interest.

It follows that the weak hydrogen bond method of determining the PA value can be recommended both from the point of view of the quantity used to characterise the protonic centres and of the precision obtainable. All three methods rely on doubtful assumptions, of which the least satisfactory are:

1) the assumed equality of the scales of "influence" of the pK_a values of acids and bases on $\Delta\nu_{OH}$ [91,92] in the strong hydrogen bond method, which seriously restricts the general validity of Eqn.(10), and

2) the need to define three groups of acids (I–III in Fig.4) in describing the dependence of pK_a on P_i. On the other hand the main assumption of the third method (which is made also in the second method) that the dependence of P_i on PA^{acid} is the same for P_i values obtained in non-aqueous solutions and in the adsorption of bases on solid acids appears to be confirmed, since the $\Delta\nu_{OH}$ values obtained in the gas phase are not very different from those obtained in solutions from ν_{OH}^{0} and ν_{OH}^{B} measurements in the same solvent.

b) *Determination of the concentration of protonic centres.* The concentration of protonic centres can be determined in various ways during the measurement of the strength of the centres by the hydrogen bond method. The simplest consists in measuring the integral intensity or the optical density of the ν_{OH} bands (in arbitrary units, normalised for $\rho = 1$) before interaction with the molecules of the base B. This approach has been used[30,31] to study the influence of the composition of zeolites on the concentration of hydroxyl groups: the result was that OH groups with $\nu_{OH} = 3640$ cm^{-1} are involved in the catalytic action of these materials. In a study of the acidic and catalytic properties (towards the formation of acrylonitrile) of TiO_2–Sb_2O_5 oxide catalysts the changes in the D/ρ ratio for the ν_{OH} bands showed that the concentration of acidic OH groups ($\nu_{OH} = 3730$ cm^{-1}) decreases as the concentration of Sb_2O_5 increases, and that the catalytic reaction on these centres is mainly in the direction of destructive oxidation of propene[52]. Thus even this very simple approach can yield important information on the nature of the catalytically active centres.

In some cases (for example, in amorphous alumino-silicate systems) OH groups of different strength have almost identical ν_{OH} values and the measured intensity of the band corresponds to the total number of centres. In this case the changes in concentration of the different centres can be monitored by measuring the intensity of the OH stretching vibration bands, which are shifted by the formation of an H bond with a B molecule (ν_{OH}^{B}). This type of analysis is reported in Ref.104.

† This term denotes the surface of any solid containing acidic OH groups.

The absolute concentration of OH groups can be determined when the integral molar absorption coefficients (A_0) of the ν_{OH} bands are known. Unfortunately, these coefficients are known only for a very few substances at present. Hughes and White[28] found that the A_0 value for the ν_{OH} 3640 cm^{-1} band of HNaY zeolite is 12.2 cm $\mu mole^{-1}$, whereas for the 3550 cm^{-1} band it is 19.5 cm $\mu mole^{-1}$. For Aerosil the value $A_0 = 9.8$ cm $\mu mole^{-1}$ has been reported[105].

The total number of OH groups can be deduced from the weight loss of the catalyst after heat treatment[18], but it may be difficult to distinguish the true surface OH groups from the co-ordinated or physisorbed water. The concentration of surface OH groups accessible to adsorbed molecules can be identified by specific chemical reactions for water: these methods are fully discussed in Ref.106. However, this approach only gives the total number of OH groups, and even if combined with a full analysis of the spectra it cannot yield the A_0 coefficients for the different classes of OH groups.

A determination of A_0 for the OH groups of zeolite by "titration" with pyridine and piperidine has been reported[28]. Unfortunately, when the strength of the protonic centres was insufficient to form the pyridinium ion, or if the centres were not accessible to the pyridine molecules, or in the presence of a large number of aprotic centres, the method was found to be inapplicable. Methods relying on H–D exchange can also be used. Knowing the total amount of deuterium in the cell, and the degree of exchange of H by D in the OH groups when the isotope exchange reaction comes to equilibrium, the concentration of OH groups can be calculated. A detailed account of these methods is given in Ref.107.

When the concentration of OH groups has to be inferred from the intensity of the stretching vibration bands of the hydroxyl groups (shifted by hydrogen bond formation) the dependence of A_0 on $\Delta\nu_{OH}^{B}$ must be known. There is substantial evidence[82,89,90,99,100,105] of the existence of a functional relationship between ΔA_0 (where $\Delta A_0 = A_0^{H\text{-bond}} - A_0$) and $\Delta\nu_{OH}^{B}$ for a wide range of acids and bases.

3. The Ion Pair Method

a) *Physicochemical basis of the method.* As was pointed out above, the ion pair method consists in studying the transfer of a proton to the adsorbed base with formation of an ion pair, which can be represented by reactions (V) and (VI) followed by association of the A^- and HB^+ ions. Therefore the heat of protonation of the base on the surface can be described by the expression

$$Q_{IP} = PA^{base} - PA^{acid} - \Delta H_{ass}. \qquad (14)$$

Using the adsorption of pyridine on HNaY zeolite as an example we shall examine the possible contributions of the various terms to the parameter Q_{IP} (according to the data in Ref.108, $Q_{IP} = 170$ kJ $mole^{-1}$). For pyridine PA = 912 kJ $mole^{-1}$ (Table 3), and for the acidic centres of the zeolite the PA found by the weak hydrogen bond method is 1200 kJ $mole^{-1}$. Hence Eqn.(14) gives $-\Delta H_{ass} = 460$ kJ $mole^{-1}$, which is comparable (in order of magnitude) to the PA of the base.

In a series of chemically similar catalysts interacting with the same base we can expect ΔH_{ass} to be almost constant. In this case the difference between the Q_{IP} values for two catalysts will be approximately equal to the difference between PA values of their OH groups.

An approach essentially similar to the above was first discussed in Refs.53 and 109. Direct measurements of Q_{IP} can be made calorimetrically[2], though the type of centre on which the probe molecules are adsorbed cannot be identified without spectroscopic control. We have suggested[108] a method of measuring Q_{IP} for pyridine by analysing the ν_{OH} bands of the surface OH groups (the IPT method). From the change in intensity of the stretching vibrations of the free OH groups the adsorption isobars of pyridine on HNaY zeolite and on zirconium phosphate were measured at 4 mmHg pressure and temperatures between 423 and 723 K. The heat of protonation of pyridine on zeolite was 170 ± 15 kJ $mole^{-1}$, and on zirconium phosphate 65 ± 10 kJ $mole^{-1}$.

Historically, however, the first method used to study the proton-donor properties of solid acids was the indicator method outlined above[4]. Since on a surface the protonated indicator consists of an ion pair with an oxygen anion (rather than, as in a solution, of an ion solvated by solvent molecules) we shall classify this method as one variant of the IP method. The basic propositions of the indicator method are fully described by Benesi[5,110], and his method of visually determining the protonation of the indicator from the change in colour of the system was used by later workers almost without change. We shall only refer to publications containing new view-points or results. Refs.111 and 112 appear to be the first report of an attempt to analyse quantitatively the relationship between the H_0 value of the OH groups on catalyst surfaces and the rate constants of heterogeneous chemical reactions.

At about the same time it was found[113,114] that in some systems (for example, zeolite cracking catalysts and alumina–silicas) the Hammett indicators cannot distinguish between protonic and aprotic centres and give the same colour for both. It was suggested that the acidity of proton-containing surface centres could be determined by using indicators which form carbonium ions on the surface, the strength of the centre being calculated by the function

$$H_R = -\lg a_{H^+} + \lg a_{H_2O} + \lg (f_{R^+}/f_{ROH}) \qquad (15)$$

Similar problems stimulated other workers[115,116] to improve the indicator method by abandoning the visual observation of colour changes, and replacing it by measurements of the diffuse reflectance spectra of the catalyst surface covered with an adsorbed base. The same workers[115,116] were the first to use an indicator adsorbed not from solution in a non-polar solvent but from the gas phase. A more detailed discussion of this approach is given in Ref.117. Both in that work, and in later work[118], the strength of the acid centres was determined from the minimum value of pK_a for the base being protonated, the second term in Eqn.(5) being either ignored without comment or assumed[118] to be close to unity. However, the assumption appears to be incorrect[117], and in general the $[BH^+]/[B]$ term in Eqn.(5) can be quite small, making the H_0 value determined as $H_0 = pK_a^{base}$ much too low and the acidity of the OH groups on the surface much too high. We should stress that equating pK_a for the acid to pK_a for the indicator is legitimate only when the number of molecules of the base B in the system is equal to the number of OH groups, and the latter are 50% ionised. In practice no attempt is made to check whether these conditions apply. The first attempt to allow for the concentration term in Eqn.(5) led to the conclusion[119] that the pK_a scale of the base is not a suitable basis for measuring the acidic properties of the surface.

We have recently described[120,121] the development of an i.r. spectroscopic method of identifying the formation of an ion pair. Its main advantage over methods in the u.v. and the visible region of the spectrum is that the formation of

ion pairs, their adsorption on aprotic centres, and the formation of a hydrogen bond by the B molecules are all readily distinguished by their i.r. spectra, so that in principle the concentrations of BH^+ and B can be measured by analysing the intensities of the ν_{OH} bands and the characteristics of the bands in the spectrum of BH^+. However, in practice the calculation of $[BH^+]/[B]$ from the i.r. spectra is complicated by the lack of reliable data on the extinction coefficients (or on A_0) for the characteristic bands of the various adsorbed forms of the base B.

We should stress that the principles of Benesi's method were not questioned in any of the investigations mentioned above (except Ref.119). Though many of the results obtained made the method appear incorrect (see references quoted by Deeba and Hall[122]) no attempt was made to analyse the discrepancies before the paper[122] drew attention to them. It should not be forgotten that the indicator method of measuring acidity postulates not only constancy of the ratio f_B/f_{BH^+} but also maintenance of the equilibrium $B_{ads} + H^+ \rightleftharpoons BH^+_{ads}$ at all times, and independence of H_0 on the concentration of B. Accurate quantitative work[122] showed that on a surface this equilibrium is not reached. Taking a strong base (n-butylamine) in an amount much smaller than the total number of OH groups on the surface we find that the molecules of the base do not distribute themselves over the surface so as to be protonated by the most acidic centres: they remain on the acidic centres (both strong, and weak) with which they first came into contact. Similar effects occur with other bases. Therefore the amount of base which is protonated depends (among other things) on the physical conditions of the experiment (temperature, flow rate and amount of B, size of pores on the surface, etc.). These effects explain the reported discrepancies[119], and they suggest that the alternative approach to the study of catalyst surfaces should be preferred[4,5,110].

It has been pointed out[122] that the strength of acidic centres could be measured from the heat of desorption of a base (E_d) previously adsorbed on the surface (the adsorption being irreversible at the given temperature). The concentration of centres having different strengths can be estimated from the amounts of irreversibly adsorbed molecules of base B of different basicity. This approach is a natural development of the calorimetric method proposed earlier (see Ref.123, and list of references in Forni's review[3]).

Thus the H_0 values of the acidic centres on the surface obtained by the ion pair method need critical scrutiny. They are unacceptable as a measure of the acid strength of a surface centre. At best they can give an indication of the relative acidity of the centre. Isolated examples[2,118,124] of the successful use of this method can be explained by the fortuitous similarity of the concentrations of acidic centres on the different catalysts, the use of compounds of a given class as probe molecules, and the constancy of the indicator adsorption conditions, the aim of the experiment in every case being not to produce reliable values of H_0 but to assign a given solid acid correctly within a series of similar compounds in order of increasing acid strength.

The shortcomings of the proposed[122] method of determining the acid strength and the number of centres of a given strength include the failure to distinguish between the different adsorption forms of the molecules of the bases B. If the base is adsorbed irreversibly also on the aprotic centres at ordinary temperatures, its desorption from those centres may invalidate the results of the measurement of the heat of desorption from the H-centres. Furthermore, E_d is not so universal a parameter as the PA.

We therefore consider the most promising approach to be a combination of measurements of heat of adsorption (or desorption) and of measurements by i.r. spectroscopy of the number and nature of different compounds formed by the B molecules with the surface centres. Since the relative precision of the measurement of Q by the IPT method is ±10% the method could advantageously be combined with more accurate, purely calorimetric measurements. The advantages of using i.r. spectral methods are even more evident in studies of reaction mechanisms for different bases on catalyst surfaces.

A convenient indication of the formation of ion pairs is obtained by using nitrogen bases (Nos.21-37 in Table 3), because protonated amines and pyridines are easily distinguished from the unprotonated bases by their i.r. spectra. On the other hand, since these bases can also form D–A complexes with L centres (which are invariably present on the surface), and since the i.r. spectra of these complexes[28] are often similar to those of protonated bases, the identification of the formation of ion pairs is only seldom unambiguous. Clear identifications have been made only by using ammonia, pyridine[18,23], and some derivatives of pyridine[121]. The use and the properties of some other probes are discussed in Refs.125–127.

b) *Determination of the concentration of protonic centres.* In studies of protonic centres by the IP method the concentration of the centres can be determined not only from the intensity of the ν_{OH} bands (as discussed above) but also from the intensity of the bands of the BH^+ ions. Hughes and White[28] have measured the A_0 coefficient for the 1540 cm^{-1} band, assigned to the pyridinium ion. By using A_0 values we can determine the concentration of proton centres on zeolites and zeolite-containing catalysts.

The integral absorption coefficients for some absorption bands of 2,6-lutidine adsorbed on protonic centres have been measured[29]. We should note that in practical studies of adsorption all the protonic centres should be filled (if the stoichiometry of the interaction is known). The possibility of departures from the stoichiometric OH : B ratio of 1 : 1 has been demonstrated[33]. In some cases the role of the protonic centres in catalytic reactions can be identified simply by studying the dependence of the intensity of the 1540 cm^{-1} band of adsorbed pyridine on the preparation conditions of catalysts of a given composition or of a series of catalysts of different composition but similar properties [30–32].

4. Method of Calculating the Strength of Protonic Centres on the Scale of the Activation Energy of the Proton Transfer Process

The method proposed[79–81,128] for determining the activation energy of the transfer of the proton (E_a^H) from the acidic centre to the base in the H-complex assumes that the dependence of the potential energy of the system on the O–H distance can be fitted by a Morse function, and that the distribution of vibrational levels can be described in the isolated diatomic molecule approximation. In this case the energy needed for complete removal of the hydrogen from oxygen (i.e. the dissociation energy) is given by the expression

$$D_0 = \frac{\omega_e}{4x} - \frac{\omega_\varepsilon}{2} \qquad (16)$$

where x is the anharmonicity coefficient [$x = (2\omega_{0\to1} - \omega_{0\to2})/2\omega_e$], ω_e is the harmonic frequency ($\omega_e = 3\omega_{0\to1} - \omega_{0\to2}$), and $\omega_{0\to1}$ and $\omega_{0\to2}$ are the observed frequencies of the fundamental i.r. transition and of the first overtone (in the symbols used in Ref.128). It is also assumed that these expressions can be used to determine the dissociation energy of the hydrogen in the -O-H...B complex ($D_{0,\mathrm{eff}}$), and that $D_{0,\mathrm{eff}}$ is the upper limit of E_a^H. The parameter $D_{0,\mathrm{eff}}$ was calculated for several H-complexes of Aerosil with different bases: with bases having PA < 700 kJ mole^{-1} ($\Delta\nu_{OH} \leq 70$ cm^{-1}) the perturbation of the O-H bond is slight and $D_{0,\mathrm{eff}}$ is independent of the strength of the base. At the same time with bases whose PA lies between 700 and 850 kJ mole^{-1} ($\Delta\nu_{OH} \cong$ 200-350 cm^{-1}) $D_{0,\mathrm{eff}}$ was found to decrease with increase of PA. It was shown that varying the base has little effect on ω_e, and it was suggested that ω_e should be treated as a constant, thus allowing $D_{0,\mathrm{eff}}$ to be calculated simply from the correlation between E_a^H and $\Delta\nu_{OH}$. By using the latter approximation the $D_{0,\mathrm{eff}}$ values were obtained for several H-complexes of bases with the OH groups of Aerosil (505 kJ mole^{-1}) and zeolite (545 kJ mole^{-1}), and compared with the activation energies of proton transfer calculated from catalysis data. The activation energy of the deuterium-hydrogen exchange on OH groups is 105-118 kJ mole^{-1}: the calculated value of E_a^H for this reaction is 126-146 kJ mole^{-1}.

Data on the adsorption of various amines and isobutanol have also been compared. In the adsorption of n-butylamine on Aerosil[120] $\Delta\nu_{OH}$ is 1050 cm^{-1} and in the adsorption of pyridine on HNaY zeolite[120] it is 1250 cm^{-1}. The interaction of the alcohol with zeolite[120] shifts ν_{OH} by 1000 cm^{-1}. The calculated values[79-81] of the three paramters lie in the range $E_a^H = 68$-78 kJ mole^{-1}, whereas the experimental values of the activation energy of proton transfer from zeolite are $\leq$8 kJ mole^{-1} for pyridine and 88 kJ mole^{-1} for the alcohol[120]. n-Butylamine is not usually protonated on Aerosil.

Thus calculations by this method for both large ($\geq$1000 cm^{-1}) and small ($\leq$70 cm^{-1}) values of $\Delta\nu_{OH}$ are inconsistent with experiment. For large values of $\Delta\nu_{OH}$ this discrepancy may be due to the inadequacy of the diatomic molecule approximation when applied to strong H-complexes. In the intermediate range of $\Delta\nu_{OH}$ values the method gives reasonable values of E_a^H.

In conclusion we note that in spite of the useful information on the ability of a catalyst to interact with a stated substance implicit in a knowledge of E_a^H this quantity is largely determined by the properties of the adsorbate and cannot be used as an independent measure of the acidic properties of the surface. Of course, solid acids can be arranged in order of increasing proton-donating power in terms of their E_a^H values for the same base B. However, the data needed for this assignment are not available, and in any case such a sequence could make the base B a model compound for acids which (for various reasons) do not catalyse its reactions, thus depriving the criterion of its main advantage. Lastly, of course, the mechanism of the reaction must be known before E_a^H can be meaningfully used.

For these reasons we consider the thermodynamic methods to be the only acceptable approach to the solution of these problems, since they allow the acidic properties of the surface to be calculated in terms of a constant which characterises the substance. We believe this information to be an essential basis of any mechanism used to explain the effect of the composition and structure of catalysts on their surface properties. The kinetic approach can also be useful, but only at the stage of detailed study of the mechanism of a specified catalytic reaction.

IV. METHODS OF STUDYING BASIC CENTRES

1. General Formulation of the Problem

The interaction of acids with basic centres (like the interaction of bases with acidic centres) probably takes place in two steps:

$$HX + B_s \to B_s \ldots HX \to B_s H^+ \ldots \bar{X} \qquad \text{(VII)}$$

By analogy with the determination of the acidic properties, the basicity of a surface can be studied by the H-bond method and by the IP method. It is again convenient to characterise the strength of the centres through their PA, and to use the pK_a values only within defined groups of acids.

Thus all the statements made in the above discussion of acidic centres are equally valid (*mutatis mutandis*) in the study of the basicity of surfaces. A suitable choice of probe molecule is extremely important in the development of accurate methods of studying the base properties of catalyst surfaces. The use of carboxylic acids and phenols is complicated by a number of factors. Firstly, the acids and phenols have fairly well developed acceptor properties (pK_a between -7 and -4,[77] PA = 750-800 kJ mole^{-1} [59]) which allow them to form D-A complexes with aprotic centres. Secondly, the most commonly used adsorbents and catalysts have surface OH groups whose i.r. absorption bands overlap the ν_{OH} bands of the acids and phenols which are sensitive to the interaction with B_S. Thirdly, if strong protonic centres are present on the surface they can cause the formation of surface esters[129], with spectral characeristics similar to those of the surface complexes of B_S with acids or phenols.

The proton-acceptor properties of surfaces can be assessed by using NH acids (in particular, pyrrole[130]), which form hydrogen bonds with the basic centres on the surface. However, the high proton affinity of the pyrrole nitrogen can cause complications (interaction of the nitrogen with the OH groups).

We have shown[131] that CH acids (in particular, $CDCl_3$) can be used as probes. The method relies on the ability of $CDCl_3$ to form H-complexes with bases[82,132]. The main advantage of this method is that hydrocarbons and their halogen derivatives are weak bases, and their interaction with aprotic or protonic surface centres is negligible. Furthermore, the νCH (or νCD) bands do not overlap the bands of the surface OH groups, and therefore the complexes of the probes with the basic centres are easily indexed.

Thus only the H-bond method has been widely used so far, and mainly in experiments with $CDCl_3$. The ion pair method has not been developed towards the study of basic centres. On the whole the search for suitable probes and the development of new methods of investigation present more serious difficulties in the study of basic centres than for protonic or aprotic (acid) centres.

2. Physicochemical Basis of the Method

By using published data[133,134] we have established[131] a correlation between the pK_a values of bases and $\Delta\nu_{CD}$ for deutero-chloroform. The relationship has been used as a calibration plot to determine pK_a for basic surface centres, and it was found that the strength of basic centres in oxides increases in the series γ-Al_2O_3 < MgO $\cong$ BeO < CaO. At least two types of centre were shown to be present on the surface of these oxides: weak basic centres, possibly consisting of OH groups, and strong centres, thought to be associated

with the presence of a bridging oxygen atom M–O–M. By using the pK_a scale the basic properties of Fe/Sb catalyst were investigated[26], and two types of centre were again identified.

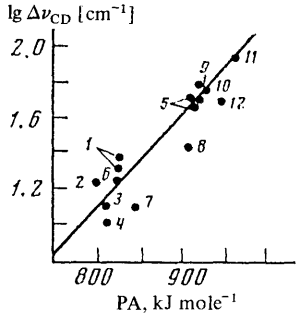


Figure 9. Dependence of $\lg \Delta\nu_{CD}$ ($\Delta\nu_{CD} = \nu_{CD} - \nu_{CD}^{gas}$) for deutero-chloroform on the PA of bases forming a hydrogen bond to it. The data[60,70,71,133–135] are for: *1*) diethyl ether, *2*) dioxan, *3*) ethyl acetate, *4*) acetone, *5*) pyridine, *6*) tetrahydrofuran, *7*) ammonia, *8*) methylamine, *9*) dimethylamine, *10*) trimethylamine, *11*) triethylamine, *12*) 2,6-dimethylpyridine. The points *1*, *5*, and *9* are typical examples of the scatter of published $\Delta\nu_{CD}$ data.

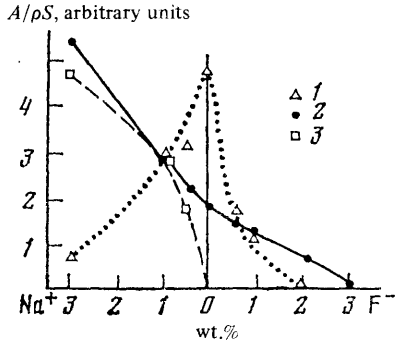


Figure 10. Variation of the relative concentrations ($A/\rho.S$) of basic centres on γ-Al_2O_3 samples modified by Na^+ or F^- ions for different PA values: *1*) 897, *2*) 810, *3*) 927 kJ mole^{-1}.

An attempt to extend the observed correlation[131] between the $\Delta\nu_{CD}$ values and the pK_a of the bases to $\Delta\nu_{CD}$ data from Ref.135 showed that methylamine and ammonia (i.e. bases from groups III and IV) cannot be included in the correlation. However, the data can all be included in a unified relationship if $\Delta\nu_{CD}$ is plotted against the PA of the base. The dependence (Fig.9) is described by the logarithmic equation

$$\lg \Delta\nu_{CD} = 0.0057\,PA - 3.54 \qquad (17)$$

which can be used to determine the PA of the basic centres. The deviation of the $\Delta\nu_{CD}$ values from the correlation curve is less than 15 cm^{-1}.

3. Determination of the Concentration of Basic Centres

Absolute integral intensity data for the $\Delta\nu_{CD}$ bands of adsorbed deutero-chloroform are not available. Therefore, by using the apparent integral intensity of the ν_{CD} band normalised to $\rho = 1$ we can only determine relative concentrations of basic centres of a given strength (i.e. centres having the same ν_{CD} frequency). This simple approach can be very useful, for example in studying the effect of treating Al_2O_3 catalysts with acids or alkalis. Plots of the intensity of the ν_{CD} bands in the spectrum of adsorbed $CDCl_3$ against the type of modifying additive are shown in Fig.10: we note that the addition of Na^+ increases the concentration of basic centres with a PA = 810 kJ mole^{-1}, while centres with PA = 897 kJ mole^{-1} disappear, and new centres with PA = 927 kJ mole^{-1} are created. The addition of F^- lowers the concentration of both strong and weak basic centres, though the effect on the former (PA = 897 kJ mole^{-1}) is more marked. No other method of obtaining this type of detailed information on the properties of basic centres exists.

V. CONCLUSIONS

The results discussed in this review show that the i.r. spectroscopy of adsorbed molecules is a revealing method of studying quantitatively the acidic and the basic properties of surfaces. By using the method with an appropriate choice of probe molecules, and by establishing the functional relationships between the normal vibration frequencies which are sensitive to the interaction with the surface centres and the thermodynamic characteristics of this interaction, we can determine the strength of the protonic, aprotic, and basic centres. The concentrations of acidic centres can be determined also by combined i.r. and adsorption measurements.

According to our experience, the following sequence of operations can be recommended for rating the acid–base properties of substances.

1) Carry out the adsorption of benzonitrile, and from the position of ν_{CN} in the absorption spectrum determine the number and type of cations acting as aprotic centres.

2) Carry out the low-temperature adsorption of CO, and measure the strength of the aprotic centres on a heat of adsorption scale. Using published data on A_0 for ν_{CO} calculate the number of aprotic centres.

3) Determine the number of different types of protonic centre from the i.r. absorption spectra of the OH groups on the surface of the sample.

4) Carry out the adsorption of a suitable weak base, and by using Eqn.(13) calculate the PA of the protonic centre. Carry out the adsorption of pyridine at different temperatures and from the intensity of the 1540 cm^{-1} band determine the number of H-centres (if PA $\leq$ 1300 kJ mole^{-1}). From the temperature dependence of the band intensity find the heat of absorption and the PA for the H-centres.

5) Carry out the adsorption of $CDCl_3$. Determine the number of types of basic centre, and calculate their PA values from $\Delta\nu_{CD}$. From the integral intensity of the ν_{CD} bands determine the relative numbers of different basic centres.

The further development of methods for the quantitative characterisation of the acid–base properties of surfaces should, in our view, proceed along the following directions: firstly, measuring the integral absorption coefficients for

the characteristic bands of the most commonly used probe molecules, and also for the individual stretching vibration bands of different types of OH group; secondly, extending the range of probe molecules which can be used to identify different types of centre; thirdly, establishing the correlations between the acid–base and the catalytic properties of catalyst surfaces (thus stimulating the practical application of these methods in heterogeneous catalysis).

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Hydrochlorination of Unsaturated Compounds

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The mechanism of the hydrochlorination of unsaturated compounds in condensed media is considered on the basis of modern data concerning the kinetics and products of the reaction and also the intermolecular interactions in the reaction system. It is shown that, like other addition processes, hydrochlorination can be carried out in non-polar media at low temperatures without the intermediate formation of ionic species, i.e. via a molecular mechanism. The factors which determine the competition between the ionic and molecular process mechanisms are analysed in detail.
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I. INTRODUCTION

The study of the addition of hydrogen halides to multiple bonds promoted the formulation of the fundamental concepts of modern chemistry. On the basis of the investigation of these reactions, ideas were developed concerning the involvement of carbonium ions and π-complexes in chemical reactions and have been used to formulate the familiar Markovnikov rule.

Hydrochlorination processes are of great theoretical and practical importance. The catalytic addition of hydrogen chloride to unsaturated compounds constitutes the basis of the large-scale syntheses of organochlorine products: ethyl chloride, vinyl chloride, methylchloroform, etc. Despite the large number of studies in this field, the process mechanism has been investigated inadequately. This is partly associated with the difficulty of obtaining reproducible kinetic data due to the catalytic influence of microimpurities on the rate and mechanism of the reaction.

The addition of hydrogen chloride to multiple bonds is usually considered mainly from the standpoint of an ionic mechanism[1,2]. Ideas concerning the ionic mechanism of the addition of halogen and hydrogen halides were formulated in the 1920's and have been developing vigorously up to the present time. On the other hand, many experimental facts do not fit within the framework of the traditional ideas. The possibility of hydrohalogenation without the preliminary ionisation of the reactants, i.e. via a molecular mechanism, has been noted by Shilov[3]. The high rate of addition at low temperatures in non-polar solvents and in the solid phase is consistent with the molecular mechanism[4]. Evidence in favour of the molecular mechanism of hydrohalogenation has been obtained in recent years in a number of investigations[5-7].

Thus the traditional ideas about the ionic mechanism of the addition of hydrogen chloride to olefins are of limited applicability. There is no doubt that the ideas formulated concerning the mechanism of electrophilic addition reactions, including hydrochlorination, will require re-examination and revision.

The mechanism of the hydrochlorination of olefins in the condensed phase is considered in the present review on the basis of modern data for the kinetics and products of reaction and also the intermolecular interactions in the hydrogen chloride–unsaturated compound–catalyst–solvent systems. The factors determining the competition between the ionic and molecular hydrochlorination mechanisms are analysed in detail. As regards the gas-phase process, only data necessary for the discussion of the general aspects of hydrochlorination are examined. Among unsaturated compounds, attention has been concentrated on olefins.

II. PRODUCTS OF THE HYDROCHLORINATION OF UNSATURATED COMPOUNDS

1. Addition to Asymmetric Compounds

In the liquid phase the majority of unsaturated compounds slowly combine with hydrogen chloride. In the presence of catalysts, hydrochlorination takes place at a high rate at room and lower temperatures[8-10]. The most reactive olefins—3,3-dimethylbut-2-ene, 2-methylbut-2-ene,[11] and isobutene[12]—readily react with hydrogen chloride in the solid phase at low temperatures. The mode of addition to asymmetric compounds is determined by the Markovnikov rule in the absence of radical initiators: "the halogen adds to the least hydrogenated carbon atom, i.e. the atom subject to the greatest extent to the influence of other carbon moieties".[13] This rule holds in the gas[14] and solid[12] phases. Some examples of the validity of the Markovnikov rule in the liquid phase are presented below[15-22]:

$$CH_3CH=CH_2 \xrightarrow{HCl} CH_3CHClCH_3 ;$$
$$(CH_3)_2C=CH_2 \rightarrow (CH_3)_3CCl ;$$
$$CH_3CX=CH_2 \rightarrow CH_3CXClCH_3 ;$$
$$CH_2=CHCl \rightarrow CH_3CHCl_2 ;$$
$$(CH_3)_2C=CHCH_3 \rightarrow (CH_3)_2CClC_2H_5 ;$$
$$CH_3C(C_2H_5)=CH_2 \rightarrow (CH_3)_2CClC_2H_5 ;$$
$$C_6H_5CH=C(CH_3)_2 \rightarrow C_6H_5CH_2CCl(CH_3)_2 ;$$
$$CH_3C\equiv CH \rightarrow CH_3CCl=CH_2 \rightarrow CH_3CCl_2CH_3 ;$$
$$CH_3CH=CHCH=CH_2 \xrightarrow{DCl} \begin{cases} \rightarrow CH_3CH=CHCHClCH_2D ; \\ \rightarrow CH_3CHClCH=CHCH_2D . \end{cases}$$

If there are two different alkyl substituents at the double bond, then both possible addition products are formed in approximately equal amounts[23]. If one of the substituents is aromatic, then chlorine adds to the carbon atom linked to the aromatic ring. Thus, $C_6H_5CHClCH_2CH_3$ is obtained from $C_6H_2CH=CHCH_3$ [24] and $C_6H_5CCl=CHCH_3$ is obtained from $C_6H_5C\equiv CCH_3$.[25]

The addition of hydrogen halides to compounds containing simultaneously a double and a triple bond has been examined[26]. As a rule, the triple bond reacts more readily than the double bond. In the presence of a deficiency of hydrogen halide, vinylacetylene and allylacetylene give rise exclusively to products of addition to the triple bond.

Addition contrary to the Markovnikov rule (anomalous addition) is not characteristic of hydrogen chloride. The photochemical hydrochlorination of dodec-1-ene yields 10–30% of the anomalous addition product and 70–90% of the normal product[27]. 1-Chloropropane is formed as a side product in the high-temperature hydrochlorination of propene[28]. Small amounts of anomalous products have been obtained in the presence of peroxides[16]. The efficiency of the action of peroxides depends on the choice of solvent, the reactant ratio, and the nature of the unsaturated compound[29]. The yield of the anomalous addition products increases after the introduction of electron-accepting substituents into the molecule. Thus the contribution of the anomalous process is 12% for propene and as much as 29% for 3-chloropropene[30]. Addition contrary to the Markovnikov rule is associated with the involvement of radicals in the reaction. In contrast to the analogous reactions of hydrogen bromide, a quantitative yield is not observed in hydrochlorination.

Anomalous addition to acetylenic hydrocarbons under the influence of catalysts is attributed to the participation of organometallic compounds[31,32].

The Markovnikov rule formally breaks down in the hydrochlorination of 3,3,3-trifluoropropene in the presence of aluminium halides[33,34]. The formation of $CF_3CH_2CH_2Cl$ is associated with the high electronegativity of the CF_3 group and agrees with the modern interpretation of the Markovnikov rule[35].

The interaction of equimolar amounts of hydrogen chloride with diene compounds leads to the formation of 1,2- and 1,4-addition products. Under mild conditions (at low temperatures), 1,2-addition predominates in the absence of catalysts. Thus at 193 K but-1,3-diene reacts with HCl to form about 80% of the 1,2-addition product[36]. The hydrochlorination of isoprene in nitromethane at 198 K leads to the exclusive formation of 3-chloro-3-methylbut-1-ene.[19] 3-Chloro-1-phenylbut-1-ene has been obtained from 1-phenylbutadiene[37]. The formation of 1,4-addition products is promoted by an increase of temperature, an increase of the polarity of the medium, and the addition of water[22,38]. The reactions of dienes with hydrochloric acid in aqueous solutions lead to 1,4-addition[39–42]. In the hydrochlorination of dienes, the 1,2-addition products are probably formed initially and subsequently isomerise to the thermodynamically more stable 1,4-addition products[43,44].

The hydrochlorination of allene and many of its derivatives takes place in accordance with the Markovnikov rule[45,46]:

$$CH_2{=}C{=}CH_2 \xrightarrow{HCl} CH_2{=}CClCH_3 \xrightarrow{HCl} (CH_3)_2CCl_2 .$$

An exception is phenylallene[47] and allene homologues having two substituents at the double bond[46], a characteristic feature of which is protonation at the central carbon atom. A characteristic feature of allene is the formation of cyclic compounds together with the usual addition products[48,49]. Cyclodimerisation in the interaction with hydrogen chloride is characteristic also of certain acetylene derivatives[50–52].

Hydrochlorination may be accompanied by a rearrangement of the carbon chain of the organic compound in the intermediate stages of the process where the structure of the addition products does not correspond to the structure of the initial unsaturated compound. For example, the hydrochlorination of *cis*- and *trans*-1-phenylbuta-1,3-dienes yields a single product—*trans*-1-methyl-3-phenylallyl chloride[53].

The gas-phase hydrochlorination of but-1-ene in the presence of the $CaCl_2$ catalyst leads to the formation of t-butyl chloride. But-2-ene gives rise to the non-rearranged product—2-chlorobutane—under the same conditions[54].

The rearrangement of an unbranched olefin is a rare phenomenon. On the other hand, the products of the hydrochlorination of branched olefins containing a tertiary carbon atom in the α-position relative to the double bond frequently do not correspond to the structure of the initial compound. For example, two products of the reaction via the mechanism[55]

$$H_3C\diagdown\!\!\diagup CHCH{=}CH_2 \xrightarrow{HCl} \begin{cases} \rightarrow (CH_3)_2CHCHClCH_3 & (33–40\%)\ , \\ \rightarrow CH_3CH_2C(CH_3)ClCH_3 & (67–60\%)\ , \end{cases}$$

were obtained in the hydrochlorination of 3-methylbut-1-ene. A rearrangement of the carbon chain occurs in the hydrochlorination of 3,3-dimethylbut-1-ene[29,56]. The ratio of the normal and rearranged chlorides is approximately 1:1 in a non-polar medium and changes to 1:6 on passing to the polar nitromethane[55]. The hydrochlorination of chlorine-containing olefins is also accompanied by rearrangements[57]:

$$CH_2{=}CClC(CH_3)_3 \xrightarrow{HCl} \begin{cases} \rightarrow CH_3CCl_2C(CH_3)_3\ , \\ \rightarrow (CH_3)_2CClCCl(CH_3)_2\ , \\ \rightarrow ClCH_2CH(CH_3)CCl(CH_3)_2\ . \end{cases}$$

The mechanism of the rearrangement of the carbon chain is examined below (Section V). The literature data[55–57] show that the rearrangement takes place at intermediate stages of the reaction and is not associated with the isomerisation of the final product. Rearrangements of the carbon skeleton are also characteristic of the hydrochlorination of norbornene and related compounds[58–60].

Table 1. Stereochemistry of the hydrochlorination of arylacetylenes.

Hydrocarbon	Solvent	Catalyst	Yield, %		Refs.
			cis	*trans*	
$DC{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	70	30	[65]
$DC{\equiv}CC_6H_5$	CH_3COOH	—	60	40	[65]
$DC{\equiv}CC_6H_5$	CH_3NO_2	$ZnCl_2$	55	45	[65]
$DC{\equiv}CC_6H_5$	sulpholane	$ZnCl_2$	50	50	[65]
$DC{\equiv}CC_6H_5$	sulpholane	—	75	25	[65]
$CH_3C{\equiv}CC_6H_5$	CH_3COOH	—	67–78	11–19	[66]
$CH_3C{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	70	30	[25]
$C_2H_5C{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	80	20	[25]
$(CH_3)_2CHC{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	95	5	[25]
$(CH_3)_3CC{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	100	0	[67]
$C_6H_5C{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	100	0	[68]

2. Stereochemistry of the Addition of Hydrogen Chloride

The stereochemistry of the hydrochlorination products is determined by the structure of the unsaturated compound and the reaction conditions. *trans*-Addition is characteristic of acetylene and its aliphatic derivatives[61–64]. Table 1 shows that there is no trans-stereospecificity in the hydrochlorination of tolane and other arylacetylenes. The yield of the *cis*-product increases steadily with increase of the bulk of the alkyl substituent. As the solvating capacity of the solvent becomes more pronounced, the ratio of the *cis*- and *trans*-additions in the catalytic hydrochlorination of tolane approaches 1.

Data on the stereochemistry of the products of the hydrochlorination of olefins are summarised in Table 2. The characteristic features of the process stereochemistry are difficult to trace clearly. A classification of olefins on the basis of the stereochemistry of their hydrohalogenation has been proposed in a review[69], where compounds with a double bond have been divided into four groups: (1) arenes and dienes yielding *cis*-addition products; (2) cyclic olefins and olefins without conjugated bonds, for which *trans*-addition is a characteristic process; (3) bicyclic olefins forming *cis*-products; (4) α,β-unsaturated carbonyl compounds, which combine with hydrogen halides exclusively in the *trans*-position. A deficiency of this classification consists in the fact that no account has been taken of the influence of conditions on the stereochemistry of the reaction which is extremely important, as can be seen from Table 2.

Table 2. Stereochemistry of the hydrochlorination of olefins.

Olefin	Solvent	ε	*T*, K	Yield, %			Refs.
				cis	*trans*	other products	
1-Methylcyclopentene	CH_3NO_2	38.6	298	4	96	0	[55]
1,2-Dimethylcyclopentene	C_5H_{12}	1.8	273	20	80	0	[70]
1,2-Dimethylcyclopentene	C_5H_{12}	1.8	195	5	95	0	[70]
Cyclohexene	CH_3COOH	6.2	298	3—4	14—28	—	[71]
Cyclohexene	CH_3COOH	6.2	353	18	18	64	[71]
1,2-Dimethylcylohexene	C_5H_{12}	1.8	298	14	86	0	[72]
1,2-Dimethylcyclohexene	C_5H_{12}	1.8	273	8	92	0	[72]
1,2-Dimethylcyclohexene	CH_3COOH	6.2	298	37—40	6—18	42—58	[72]
1,2-Dimethylcyclohexene	CH_3COCl	15	273	76	24	0	[72]
1,2-Dimethylcyclohexene	CH_2Cl_2	8.9	298	64—74	26—36	0	[72]
1,2-Dimethylcyclohexene	CH_2Cl_2	8.9	177	88	12	0	[72]
1,2-Dimethylcyclohexene	HCl (liq.)	9.1	177	87	13	0	[73]
1,2-Dimethylcyclohexene	$(C_2H_5)_2O$	4.2	273	5	95	0	[73]
1,2-Dimethylcyclohexene	sulpholane	44	298	53	47	0	[72]
1,2-Dimethylcyclohexene	CH_3OH	32.6	298	9—30	70—91	0	[72]
$\Delta^{9,10}$-Octalin	CH_2Cl_2	8.9	195	54	46	0	[74]
$\Delta^{9,10}$-Octalin	CH_2Cl_2	8.9	177	61	39	0	[73]
$\Delta^{9,10}$-Octalin	HCl (liq.)	9.1	177	64	36	0	[73]
$\Delta^{9,10}$-Octalin	$(C_2H_5)_2O$	4.2	273	2	98	0	[73]
$\Delta^{9,10}$-Octalin	aq.HCl	—	273	6	94	0	[74]
Indene	CH_2Cl_2, C_5H_{12}	—	195	50	50	0	[75]
Acenaphthene	CH_2Cl_2	8.9	273	85	15	0	[76]
Norbornene	various	—	195	49	1	50	[58]
Apobornylene	various	—	195	90	0	10	[60]
Bornylene	various	—	195	100	0	0	[59]

The data in Table 2 agree with the above classification[69] for norbornene and other bicyclic compounds, for which only *cis*-addition does indeed occur. For indene, acenaphthalene, norbornene, and related compounds in the absence of steric hindrance in weakly polar and non-polar media, the preferential formation of the *cis*-product has been observed. The exclusive formation of the *trans*-product has not been observed for cyclohexene and cyclopentene homologues[72]. The direction of the process varies as a function of the choice of the solvent. In the case of 1,2-dimethylcyclohexene an increase of the polarity and ionising capacity of the solvent promotes *cis*-addition. It has so far been impossible to formulate a general rule governing the influence of the medium on the stereochemistry of the hydrochlorination. Treatment of the results is hindered by the influence of steric factors on addition to systems containing the cyclopentene or cyclohexene ring.

Additional possibilities for the formation of stereoisomers arise in the reactions of dienes. Thus 1,4-addition to conjugated dienes can lead to *cis*- or *trans*-alk-2-enes. The hydrochlorination of 2,3-dichlorobuta-1,3-diene[77] and *trans*-penta-1,3-diene[22] results in the formation of mainly the *trans*-isomers. Both possible products have been noted in the hydrochlorination of chloroprene[78].

Hydrochlorination at room and elevated temperature, particularly in the presence of catalysts, is frequently complicated by the polymerisation[30,36,79–83] and isomerisation[45,46,72] of the olefins as well as the decomposition of the addition products[10,84] occurring under the influence of the same catalysts. The addition of hydrogen chloride in hydroxylated solvents competes with the addition of the solvent[56,57,71,85,86].

III. KINETICS OF HYDROCHLORINATION

1. Kinetics of the Gas-Phase Reaction

Non-catalytic hydrochlorination in the gas phase takes place slowly. The reaction of isobutene with hydrogen chloride at 300–500 K is described by a second-order kinetic equation, whose rate constant can be represented in the following form[87]:

$$k_2 = 10^8 \exp(-28800/RT)\ (\mathrm{dm^3\ mol^{-1}\ s^{-1}}).$$

At high temperatures the equilibrium is displaced towards the starting materials and the kinetic parameters of the majority of the hydrochlorination processes have been calculated from data for the molecular elimination of HCl from the corresponding alkyl chlorides. The results of such calculations are presented below[14]:

Olefin	C_2H_4	C_3H_6	iso-C_4H_8
E, kJ mol^{-1}	167	141	106
lg$A$ (dm^3 mol^{-1} s^{-1})	8.8	7.8	6.1

The reactivity of olefins increases rapidly with increase of the number of substituents at the double bond. The activation energy for addition contrary to the Markovnikov rule is higher by at least 30 kJ mol^{-1} than for normal addition[14].

Extrapolation of the elimination data to room and lower temperatures leads to the conclusion that the rate of the gas-phase hydrochlorination of the majority of olefins should be negligible under such conditions. However, recent studies have shown[88,89] that the hydrochlorination of many olefins proceeds at an appreciable rate at 300 K and below and that the kinetic process parameters are different from those found earlier[14,87]. The hydrochlorination of isobutene is accelerated on passing from 373 K to lower temperatures[88]. The rate of the process is higher by a factor of 10^9 than might have been expected on the basis of data for the high-temperature process. The gas-phase hydrochlorination of allene is described by a second-order equation and takes place with zero activation energy[45]. The following equation has been obtained for the low-temperature hydrochlorination of propene in the gas phase[89]:

$$v = k_4 [C_3H_6] [HCl]^3 .$$

A negative temperature coefficient was observed in the reaction: the rate of the reaction at 293 K is three times higher than at 373 K. Traces of water, nitrogen oxides, and the surface of the vessel have a catalytic influence on the reaction; quantitative data have not been obtained for the catalytic process.

The data for the reaction kinetics permit the conclusion that in the gas phase the hydrochlorination takes place via two pathways. At high temperatures a bimolecular reaction with a high activation energy takes place. At temperatures below 373 K another pathway predominates, for which the

effective activation energies are negative or close to zero and whose rate is described by a second-order or a higher-order equation.

2. Kinetics of the Non-catalytic Reaction in the Liquid Phase

The kinetic equation for the liquid-phase hydrochlorination depends on the solvent selected. In non-polar solvents the kinetics are complex. For example, the hydrochlorination of isobutene is approximately described by the equation[90]

$$v = k_4 [C_4H_8] [HCl]^3 \ .$$

The rate of the process at 273 K is higher than at 195 K. However, it has been noted that preliminary cooling of the reaction mixture to 195 or 77 K leads to an increase of the degree of reaction on subsequent heating to 273 K. A negative temperature coefficient has been observed in the hydrochlorination of 1-methyl-2-methylenenorbornene in pentane[91]. Overall, the hydrochlorination kinetics in polar media have been inadequately investigated.

An increase of the polarity of the solvent leads in a number of instances to an increase in the rate of hydrochlorination. For example, on passing from pentane to methylene chloride, the time required for the quantitative addition of HCl to norbornene is considerably reduced[92]. Dilution of acetic acid with cyclohexane retards the hydrochlorination of 1-phenylpropyne[66]. Instances are known where an increase of the dielectric constant of the solvent ε has a weak influence on the rate of hydrochlorination. Thus in pentane and methylene chloride a specific degree of hydrochlorination of acenaphthene is attained during the same period[76]. The rate of hydrochlorination of a number of dienes depends little on the dielectric constant[93]. The retardation of hydrochlorination is sometimes observed on passing to more polar media. The rate of hydrochlorination of hex-3-ene and cyclohexene diminishes in the following sequence of solvents: heptane > xylene > nitrobenzene > ether[94]. The authors[94] attribute this influence of the medium to the electron-donating capacity of the solvents and specific solvation and not to the dielectric constant of the solvent.

The kinetic equation for hydrochlorination in polar media can be represented in the following form:

$$v = k_2 [RH] [HCl] + k_3 [RH] [HCl]^2 \ . \qquad (1)$$

The ratio of the two terms of Eqn.(1) is determined by the nature of the solvent. In highly polar solvents without hydroxy-groups such as nitromethane, the hydrochlorination of various olefins is described by an equation of third order overall[19,55,95]. The third order is characteristic of the hydrochlorination of isoprene in the absence of a third component[96]. In acetic acid both terms of Eqn.(1) are significant. The third and higher orders have been observed in the hydrochlorination of 1-phenylpropyne[66] and hex-3-yne[56]. In the case of olefins in acetic acid a termolecular hydrochlorination process competes with the bimolecular reaction. The interpretation of the reaction kinetics in acetic acid is hindered by the inadequate accuracy of the kinetic data[85]. The most reliable results appear to be those of the studies of Okuyama and co-workers[47,53], where the kinetics of the hydrochlorination of dienes were investigated over a wide range of hydrogen chloride concentrations. A change in the kinetic equation for the reaction with increase of the HCl concentration was observed. For phenylallene, the reaction is described by an equation of second order overall at an HCl concentration of 0.1–0.25 M and of third order at 0.64–1.3 M. Hydrochlorination in acetic acid is accelerated in the presence of salts containing the Cl^- anion[56,85].

The hydrochlorination of propene in organochlorine solvents is described by a second-order equation, of first order with respect to each reactant[97]. In the analysis of the kinetic equations for hydrochlorination in organochlorine solvents, it is necessary to take into account the possibility of the self-association of hydrogen chloride[98].

Table 3. Kinetic parameters of liquid-phase hydrochlorination.

Hydrocarbon	Solvent	n*	$-\Delta H$, kJ × × mol^{-1}	$-\Delta S$, J × × mole^{-1} K^{-1}	Refs.
Propene	$C_2H_2Cl_4$	2	39	162	[97]
Propene	$C_2H_3Cl_3$	2	25	229	[97]
Propene	$C_2H_4Cl_2$	2	27	213	[97]
Propene	$C_3H_6Cl_2$	2	43	160	[97]
Hex-3-yne	CH_3COOH	3.5	96	84	[56]
Hex-3-yne	$(CH_3)_4NCl+CH_3COOH$	1	60	138	[56]
Phenylallene	CH_3COOH	3	81	53	[47]
1-Phenylbuta-1,2-diene	CH_3COOH	3	74	69	[53]
cis-1-Phenylbuta-1,3-diene	CH_3COOH	3	69	22	[53]
trans-1-Phenylbuta-1,3-diene	CH_3COOH	3	89	47	[53]

*Here n is the overall reaction order.

The overall order of certain liquid-phase hydrochlorination reactions and their activation parameters are listed in Table 3. The kinetic data make it possible to identify the main types of non-catalytic hydrochlorination in the liquid phase. The processes proceed at a low rate in non-polar solvents, are described by high-order equations, and can be accelerated at low temperatures. The kinetics of hydrochlorination in non-polar media resemble those of the low-temperature gas-phase reaction. In a polar solvent the hydrochlorination process proceeds via two pathways described by second- and third-order equations. The activation energies are in this instance 25–100 kJ mol^{-1}. The relative contributions of the processes depend on the nature of the solvent and the reactants.

The reactions of concentrated hydrochloric acid, in which the main bulk of hydrogen chloride is dissociated, must be considered separately. For example, the order of the reaction of cyclohexene and methylcyclohexenes with respect to HCl is first and that with respect to the olefin is first or zero. The observed activation energies are 32–76 kJ mol^{-1}.[99] Activation energies of 4 and 10 kJ mol^{-1} have been obtained for the 1,2- and 1,4-addition respectively in the hydrochlorination of isoprene in hydrochloric acid[42].

3. Kinetics of Catalytic Hydrochlorination

Hydrochlorination is catalysed by various substances. The simplest catalyst is water. Its catalytic action has been observed in the hydrochlorination of isoprene[38], isobutene[90], and dicyclopentadiene[100]. The acceleration of the addition and the increase of the yield of the *trans*-product in the presence of water have been noted for a series of reactions in acetic acid[72,85,101]. A slight acceleration of the hydrochlorination of 3,3-dimethylbut-1-ene has been observed after the addition of water to a concentration of 0.6 M, while a further increase of its concentration to 2.5 M retards the reaction[56]. No kinetic data are available for the influence of water on the rate of hydrochlorination.

Metal halides are the most effective hydrochlorination catalysts. In the presence of the halide MX_n, the kinetic equation for hydrochlorination usually assumes the form

$$v = k_3 [RH] [HCl] [MX_n] \quad . \qquad (2)$$

It describes satisfactorily the kinetics of the hydrochlorination of ethylene in nitrobenzene[102], of vinyl chloride and the isomeric 1,2-dichloroethylenes in the presence of $AlCl_3$,[103] of propene in the presence of $FeCl_3$,[104] and of styrene in the presence of $SnCl_4$.[105] A decrease of the reaction order with respect to the olefin in the presence of an excess of the latter has sometimes been observed[104]. A decrease of the reaction order with respect to the catalyst with increase of the $SnCl_4$ concentration above 0.04 M has been noted in the hydrochlorination of styrene[105].

Overall orders in excess of the third are rarely encountered for the catalytic process. An overall fourth order, second with respect to the olefin, has been noted for the catalytic hydrochlorination of vinyl chloride under the influence of $FeCl_3$.[106] An increase of the order with respect to the catalyst occurs in the hydrochlorination of ethylene in the presence of $AlCl_3$ in organochlorine solvents[104] and of acetylene in the presence of CuCl in aqueous solution[107].

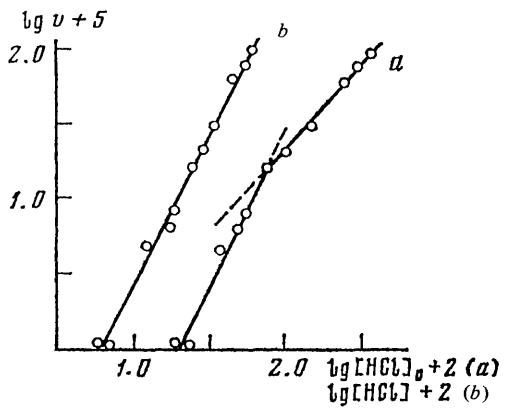


Figure 1. Dependence of the logarithm of the initial rate of hydrochlorination of cyclohexene in the presence of $SnCl_4$ in hexane at 183 K on the logarithm of the initial concentration of hydrogen chloride $[HCl]_0$ (*a*) or on the logarithm of the concentration of "free" hydrogen chloride [HCl] (*b*).[108,109]

The catalytic hydrochlorination of cyclohexene in non-polar and weakly polar media has been investigated taking into account complex formation in the system[6,108,109]. It is seen from Fig. 1*a* that the kinetics of the reaction with a variable order with respect to hydrogen chloride are described satisfactorily by the equation for a fourth-order reaction:

$$v = k_4 [C_6H_{10}] [HCl]^3 [SnCl_4] \quad , \qquad (3)$$

where [HCl] is the concentration of hydrogen chloride not bound in associated species, which can be calculated from the material balance equation

$$[HCl]_0 = [HCl] + 2K_{(HCl)_2} [HCl]^2 + K_{C_6H_{10}\cdot HCl} [C_6H_{10}] [HCl] + K_{SnCl_4\cdot HCl} [SnCl_4] [HCl] .$$

The $\lg v - \lg [HCl]$ relation (Fig. 1*b*) does not have a break and the slope of the straight line is 2. At low temperatures and high HCl concentrations, where $[HCl]^2 = [HCl]_0/2K_{(HCl)_2}$, Eqn. (3) becomes identical with the kinetic equation for a third-order reaction:

$$v = k_4/2K_{(HCl)_2} [C_6H_{10}] [HCl]_0 [SnCl_4] = k_3 [C_6H_{10}] [HCl]_0 [SnCl_4] .$$

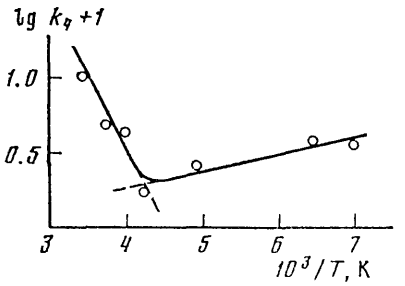


Figure 2. Dependence of the logarithm of the rate constant k_4 for the hydrochlorination of cyclohexene in the presence of $SnCl_4$ in hexane on the reciprocal of temperature[109].

Table 4. Activation energies for the liquid-phase catalytic hydrochlorination.

Hydrocarbon	Solvent	Catalyst	*E*, kJ mol^{-1}	Refs.
Ethylene	$C_6H_5NO_2$	$AlCl_3$	70	[102]
Acetylene	H_2O, NH_4Cl	CuCl	42	[107]
Propene	$C_2H_2Cl_4$	$FeCl_3$	40	[104]
Vinyl chloride	$C_2H_2Cl_4$	$AlCl_3$	56	[106]
Vinyl chloride	$C_2H_2Cl_4$	$FeCl_3$	88	[106]
cis-Dichloroethylene	$C_2H_2Cl_4$	$AlCl_3$	73	[106]
trans-Dichloroethylene	$C_2H_2Cl_4$	$AlCl_3$	84	[106]
Styrene	CCl_4	$SnCl_4$	39	[105]
Cyclohexene	C_6H_{14}	$SnCl_4$	18 *	[109]
Cyclohexene	C_6H_{14}	$SnCl_4$	0 **	[109]
Cyclohexene	CCl_4	$SnCl_4$	0	[109]
Cyclohexene	CH_2Cl_2	$SnCl_4$	14	[109]
Cyclohexene	CH_2Cl_2—CCl_4	$SnCl_4$	10	[109]

*In the temperature range 233–293 K.
**In the temperature range 143–203 K.

On passing from hexane to methylene chloride, the reaction rate increases slightly and at 183 K is almost independent of the dielectric constant of the medium.

The temperature variation of the reaction rate constant k_4 is illustrated in Fig. 2 in terms of the variables of the Arrhenius equation, the Figure showing that the activation energy for the reaction decreases with decrease of temperature.

A complex form of the temperature variation of the rate of the process has also been observed in the catalytic hydrochlorination of ethylene in ethyl chloride: at 273 and 163 K the reaction is slow, the rate of the process being a maximum at 213–218 K.[81]

In the majority of cases, the rate constants for catalytic hydrochlorination obey the Arrhenius equation. The activation energies for a number of homogeneous catalytic hydrochlorination reactions are listed in Table 4. Evidently, for

the simplest unsaturated compounds, the activation energies are 40–90 kJ mol^{-1}. For the more reactive olefins (cyclohexene and styrene), the activation energies are less than 40 kJ mol^{-1}. For cyclohexene in non-polar solvents at low temperatures, the activation energy for hydrochlorination is close to zero. In a more polar solvent (methylene chloride) the activation energy increases.

4. The Isotope Effect

The isotope effect in hydrochlorination in polar and hydroxylated media varies in the range 0.7–2.3. For example, isotope effects of 1.3 for cyclohexene[71], 1.15 for 3,3-dimethylbut-1-ene[56], 1.4 for styrene[56], and 1.54 and 2.3 for *cis*- and *trans*-1-phenylbuta-1,3-dienes respectively[53] have been obtained in acetic acid. In nitromethane, HCl adds to 1-methylcyclopentene 1.6 times more slowly than DCl.[55]

When the polarity of the medium is reduced, the ratio k_H/k_D increases. For catalytic hydrochlorination of cyclohexene (at 183 K), the isotope effect changes from 0.7 to 4.2 on passing from methylene chloride to hexane[110].

The kinetic characteristics of the hydrochlorination reactions of unsaturated compounds—a high, frequently variable, reaction order, a negative temperature coefficient, and an activation energy close to zero—may be due to the association of the reactants in the reaction system.

IV. INTERMOLECULAR INTERACTIONS IN HYDROGEN CHLORIDE–UNSATURATED COMPOUND–CATALYST–SOLVENT SYSTEMS

In systems containing hydrogen chloride, an unsaturated compound, and a catalyst in a condensed phase, a number of complex formation processes take place. The ability of hydrogen chloride to form hydrogen bonds, which leads to self-association, plays an important role.

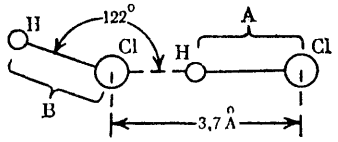
1. Self-Association of Hydrogen Chloride

The polymeric species $(HCl)_n$ are formed in all the phase states. In the gas phase, $n = 2$. The study of gaseous HCl by infrared spectroscopy showed that at 293 K and 10 atm approximately 1% of the substance exists in the form of the dimer $(HCl)_2$. The enthalpy of dimerisation is close to −10 kJ mol^{-1}.[111]

In polar and hydroxylated solvents, the complex formation reaction with the solvent suppresses the self-association of hydrogen chloride. In a non-polar inert solvent (1,2-dibromotetrafluoroethane) at an HCl concentration below 0.5 M, the dominant type of self-association is the dimerisation of HCl. The dimerisation equilibrium constant is 0.84 litre mol^{-1} at 293 K and the enthalpy and entropy of the process are −8 kJ mol^{-1} and −31 J mol^{-1} K^{-1}. The degree of self-association increases with decrease of temperature: 70% of the hydrogen chloride molecules are dimerised at 173 K for [HCl] = 0.5 M.[98]† In organochlorine solvents complex formation with the solvent competes with the dimerisation of hydrogen chloride and the degree of dimerisation of HCl decreases[98,112].

The self-association of hydrogen chloride in the solid phase has been observed in an infrared spectroscopic study of HCl in an argon matrix at 10–30 K; the spectra show bands due to the hydrogen chloride dimers, trimers, and tetramers[113–115]. In order to obtain isolated hydrogen halide molecules, a 400-fold excess of a diluent is necessary[116].

Two types of associated hydrogen chloride species—linear and cyclic—have been considered in the literature. In the trimers and tetramers all the HCl molecules are equivalent, which indicates a cyclic structure. In the dimer the HCl molecules have different force constants[115]. The study of the structure of the hydrogen chloride dimer by pulsed ^1H NMR showed that it is as follows[117]:



The distance between the hydrogen atoms is 3.3 Å. The greater stability of the linear structure compared with the cyclic structure is consistent with the results of a quantum-mechanical calculation[118]. In the dimer there is charge transfer from molecule B to molecule A. The negative charge is concentrated on the chlorine atom of the A molecule and the positive charge is distributed between the remaining atoms.

2. Complexes of Hydrogen Chloride with Unsaturated Compounds

The formation of molecular 1:1 complexes in solid mixtures of hydrogen chloride with olefins and acetylenes has been demonstrated in studies of fusion diagrams[11,119]. Complexes of the type 2HCl.RH are also known for a number of unsaturated compounds and the complexes 4HCl.RH are known for alkylacetylenes[119]. Application of low-temperature infrared spectroscopy led to the discovery of the complexes HCl.2RH.[120] The enthalpy of formation of the 1:1 complexes in the solid phase is between −10 and −22 kJ mol^{-1} according to infrared spectroscopy[121]. The contribution of pair or collective interactions to the stabilisation of such complexes is low[122,123]. The 1:1 complexes are the most stable in the solid phase[120,123].

In the liquid and gas phases these complexes have been inadequately studied. The first quantitative data were obtained as late as 1978 using low-temperature infrared spectroscopy[124,125]. In liquid nitrogen at 93 K the equilibrium constant for the complex formation with hydrogen chloride increases from 8 to 6×10^3 litre mol^{-1} on passing from ethylene to 2,3-dimethylbut-2-ene, while the enthalpy of complex formation changes from −5.8 to −13.4 kJ mol^{-1}.

The degree of charge transfer in the complexes of hydrogen chloride with olefins is considerable and amounts to 0.1 to 0.3 of a unit electronic charge[121]. There are no direct experimental data for the disposition of the molecules in these complexes. It has been suggested that the hydrogen chloride molecule is arranged at right angles to the plane of the olefin. On the basis of the satisfactory correlations between the shift of the vibration frequencies and the enthalpy of complex formation characteristic of hydrogen-bonded complexes, it is believed that the interaction in such complexes involves a hydrogen bond[122,126,127]. However, quantum-mechanical calculation by the CNDO/3 method showed

†During the preparation of this review for the press, B.Desbat and P.V.Huong published their study (Bull.Soc. chim.France, 1981, 301), in which the dimerisation of hydrogen chloride in the liquid phase was additionally confirmed by infrared and Raman spectroscopy and the structure of the dimers was considered.

that the configuration in which the hydrogen chloride molecule assumes the disposition with the chlorine atom pointing towards the olefin is the most stable[128]. The negative charge is concentrated on the chlorine atom and the positive charge is distributed over the molecule of the unsaturated compound. The calculated degree of charge transfer in the ethylene–HCl complex is close to 0.1.

Several types of orientation can probably occur in complexes of hydrogen chloride with olefins. Comparison of the experimental entropy for the formation of the ethylene–hydrogen chloride complex with the values calculated for different models of the complexes showed that agreement can be achieved only on the assumption that internal movements occur in the complex, namely rotation or vibration, with a high amplitude[129]. There is apparently no rigorously fixed molecular orientation in the complexes of hydrogen chloride with olefins and their structures are extremely labile.

3. Complexes with Participation of the Solvent

The majority of organic solvents form complexes with hydrogen chloride. We shall confine ourselves to a brief consideration of the most important types of interactions.

The formation of complexes of HCl with compounds of the benzene series was observed in a study of fusion diagrams[119] and of the solubility of gaseous hydrogen chloride in aromatic compounds[130]. The thermodynamic characteristics of the complex formation reactions are comparable to those obtained for olefins. For example, the equilibrium constant for the formation of the benzene–HCl complex at 293 K is 0.17 litre mol^{-1} and $-\Delta H = 12.5$ kJ mol^{-1}.[131] The nature of the bonding in the complexes is various. In the case of olefins charge transfer plays the main role, while for aromatic compounds dipole–quadrupole and dispersion interactions are important[126]. The higher energy of the interaction of HCl with benzene in the presence of water indicates the possibility of the formation of ternary complexes[132].

Organochlorine compounds form hydrogen-bonded complexes with hydrogen chloride[98,112,133,134]. The enthalpies of formation of such complexes are in the range between −6 and −10 kJ mol^{-1} and the equilibrium complex formation constants at room temperature are approximately 0.1 litre mol^{-1}.

Substances containing ether or carbonyl oxygen form more stable complexes with hydrogen chloride. When ethers interact with hydrogen chloride, 1:2 complexes[136] as well as associated species with three, four, and six HCl molecules[137] are formed in addition to the well known 1:1 complexes[135]. In the interaction with aromatic ethers, the coordination involves the oxygen atom[138]. The enthalpies of formation of 1:1 complexes of HCl with ethers are in the range between −23 and −30 kJ mol^{-1}.[131] The 1:2 complexes are weaker and are characterised by $-\Delta H \cong 10$–16 kJ mol^{-1}.[136] Experimental and computational studies on the structures of such complexes have been described[138,139,140]. When HCl interacts with ethers, there is a possibility of the protonation of the latter with the formation of onium salts[140,141]. However, HCl_2^- ions could not be detected by NQR in the solid phase, which is inconsistent with the hypothesis of spontaneous protonation[138].

The complexes of hydrogen chloride with other oxygen-containing compounds, including water, have been considered in a number of studies[142–146].

The universal ability of hydrogen chlorides to form complexes is indicated by the observation of intermolecular interaction of HCl with argon[147] and nitrogen[148].

The interaction between unsaturated compounds and an organochlorine solvent (CCl_4) is indicated by the increase of the negative enthalpy of mixing compared with hydrocarbons without a double bond[149]. For aromatic hydrocarbons and olefins, the enthalpies of formation of their complexes with CCl_4 are −(1–5) kJ mol^{-1}.[150]

4. Complexes of Metal Halides in Hydrochlorination

The typical hydrochlorination catalysts, namely metal halides, are strong complex-forming agents. The stability of the complexes of Group IV metal halides is low. Thus the enthalpy of formation of the complex of hydrogen chloride with tin tetrachloride in a non-polar medium is −6 kJ mol^{-1}.[112] The shifts of the stretching vibration band of HCl in $TiCl_4$ and CCl_4 relative to the gas phase are approximately the same, which indicates the similarity of the bond energies[151]. Such complexes can be formed as a result of the usual classical van der Waals interactions. The enthalpies of reaction of HCl with a number of metal halides, estimated from adsorption measurements, are −8 kJ mol^{-1} for solid $BiCl_3$, −9 kJ mol^{-1} for $ZnCl_2$, and −15 kJ mol^{-1} for $CdCl_2$.[152] The Group III metal salts form more stable complexes with HCl: the enthalpies of formation of such complexes are −16 and −41 kJ mol^{-1} for $FeCl_3$ and $AlCl_3$ respectively[104]. The most probable composition of the complex of HCl with $AlCl_3$ corresponds to the formula $HAl_2 \cdot Cl_7$;[153] the structure of the complex depends on the nature of the solvent[104,154].

The majority of metal halides form complexes also with unsaturated compounds and their strength varies within wide limits. A high stability is characteristic of aluminium halide complexes. The appreciable shift of the stretching vibration bands of the double bonds in the ethylene, propene, cyclohexene, and other olefin complexes with $AlHal_3$ indicates perturbation of the π-electron cloud[155,156]. The structure of a typical π-complex with coordination of the aluminium atom to the centre of the double bond has been proposed for such complexes. Aluminium halides are involved in complexes of this kind in a monomeric form, which indicates their stability. The equilibrium constant for the formation of the propene–$AlCl_3$ complex is 7.3 litre mol^{-1} at 293 K and the enthalpy of formation is approximately −100 kJ mol^{-1}.[104]

The complexes of Group IV metal salts with olefins are less stable; thus $K_p = 0.33$ litre mol^{-1} and $-\Delta H = 6$ kJ mol^{-1} (at 298 K) for the complex of $TiCl_4$ with isoprene[157].

Metal halides can form complexes with the majority of organic solvents[158].

Thus a wide variety of complex formation processes occur in hydrogen chloride–unsaturated compounds–catalyst–solvent systems. The most important of these are the formation of a complex by hydrogen chloride with olefins and also by the catalyst with olefins and hydrogen chloride. In concentrated solutions in non-polar media hydrogen chloride is to a large extent associated. Without studying these processes, a correct treatment of kinetic data is impossible. Complex formation is a characteristic feature of the systems considered and must be taken into account in the study of the mechanism of the hydrochlorination reaction. Complexes in which there is a significant rearrangement of the electronic structure of the molecule and comparatively strong intermolecular bonds are formed are the most important for the reaction.

V. THE MECHANISM OF THE ADDITION OF HYDROGEN CHLORIDE TO MULTIPLE BONDS

The hydrochlorination reactions can proceed via radical and molecular mechanisms. The radical addition of hydrogen chloride takes place slowly and fairly rarely[30,159–162]. This

pathway is not characteristic of hydrochlorination. The ionic and molecular mechanisms are much more important.

1. The Ionic Mechanism of Hydrochlorination

(a) *Evidence for the involvement of ions in the reaction.* The idea of the involvement of ions or ion pairs in hydrochlorination is based mainly on the results of the study of the composition of the addition products. The validity of the Markovnikov rule is typical for ionic processes; it is based on the tendency of the proton to attack the sites with the highest electron density at the C–H bonds in the olefin molecule[35]. The modern interpretation of the Markovnikov rule is based on the rapid rearrangement of primary alkyl cations to the more stable secondary cations:

$$RCH=CH_2 \xrightarrow[-Cl^-]{HCl} \left[\begin{array}{l} \longrightarrow RCH_2CH_2^+ \\ \longrightarrow RCH^+CH_3 \end{array} \right] \xrightarrow{\text{just}} \quad .$$

Quantum-mechanical calculations, including non-empirical calculations, predict that the primary cations of the type $CH_3CH_2CH_2^+$ or $ClCH_2CH_2^+$ are unstable and cannot exist under the usual conditions. They should be converted without activation energy into the more stable cations $CH_3CH^+CH_3$ or $ClCH^+CH_3$.[163] Thus the protonation is thermodynamically controlled and the Markovnikov rule can be explained within the framework of an ionic mechanism.

The involvement of ions in the hydrochlorination in hydroxylated solvents explains the simultaneous formation of solvent addition products. The carbonium ions formed in the reaction are subjected to nucleophilic attack not only by Cl^- anions but also by solvent molecules:

$$RCH=CH_2 \xrightarrow[-Cl^-]{HCl} RCH^+CH_3 \left[\begin{array}{l} \xrightarrow{Cl^-} RCHClCH_3 \\ \xrightarrow[-H^+]{R'OH} RCHCCH_3 \\ \qquad\quad | \\ \qquad\quad OR' \end{array} \right] .$$

The rearrangements of branched olefins can be attributed to rapid isomerisation reactions of the carbonium ions:

$$(CH_3)_2CHCH=CH_2 \xrightarrow[-Cl^-]{HCl} (CH_3)_2CHCH^+CH_3 \xrightarrow{\text{just}} (CH_3)_2C^+CH_2CH_3$$
$$\downarrow Cl^- \qquad\qquad \downarrow Cl^-$$
$$(CH_3)_2CHCHClCH_3 \qquad (CH_3)_2CClCH_2CH_3 \ .$$

The involvement of ionic species in a catalytic process is believed to be confirmed by the exchange of the halogen between HCl and the catalyst, which has been observed in the hydrochlorination of styrene[79]:

$$C_6H_5CH=CH_2 + HCl + SnBr_4 \rightarrow C_6H_5CH^+CH_2SnBr_4Cl^- \left[\begin{array}{l} \longrightarrow C_6H_5CHClCH_3 \ ; \\ \longrightarrow C_6H_5CHBrCH_3 \ . \end{array} \right.$$

The acceleration of hydrochlorination in polar media and also the isotope effect in the reaction close to unity, indicating that the H–Cl bond is broken in the transition state, are consistent with the ionic character of the process.

In the ionic mechanism, the hydrochlorination is treated as a stepwise process consisting of a sequence of ion or ion pair formation reactions and the addition of a nucleophilic species. According to a number of workers[1], ionisation is preceded by the formation of complexes of HCl with the unsaturated compound or the catalyst.

In the simplest case the reaction can be represented schematically as follows:

$$RH + HCl \ (\text{or } RH \cdot HCl) \underset{(a)}{\rightarrow} RHH^+Cl^- \underset{(b)}{\rightarrow} RH_2Cl \ .$$

Processes which are the reverse of reactions (*a*) do not play a significant role in hydrohalogenation, since there is no isotope exchange between olefins and deuterium halides[22,56,164]. 1,2-Dimethylcyclohexene, where the migration of the double bond indicates the reversibility of the ionisation stage, constitutes an exception[72].

(b) *The ionisation stage.* The accumulation of measurable amounts of ionised species has not been observed in hydrochlorination. Inductive periods on the product accumulation curves are not characteristic of hydrochlorination either. This suggests that the formation of ionic species is the rate-limiting stage of the reaction. Only reactions in aqueous media, where the degree of dissociation of HCl into ions is high, may be exceptions.

Ions can arise in the reaction system as a result of the interaction of Cl with the unsaturated compound or after the preliminary dissociation of HCl and the reactions of the resulting ions with the multiple bonds. The majority of organic compounds have proton affinities in the range 500 to 800 kJ mol^{-1}.[165] Ions of the protonated solvent should be formed in solution. The degree of dissociation of HCl in organic solvents is low and is usually in the range 10^{-3} to 10^{-10}%.[19,25,104,166] The dissociation is facilitated by the interaction with a second HCl molecule and the formation of the HCl_2^- ion. The dimer $(HCl)_2$ is a stronger acid than HCl. Thus the dissociation of HCl in an organic solvent(Solv) can be represented schematically as follows:

$$Solv + (HCl)_2 \underset{}{\overset{K_{(HCl)_2}}{\rightleftharpoons}} Solv\,H^+ + HCl_2^- \quad (\text{or } Solv + 2HCl \rightleftarrows Solv\,H^+ + HCl_2^-) \ .$$

This process is significant if the bond between the proton and the solvent is stronger than that between the proton and the unsaturated compound. For reactions in hydrocarbons and halogeno-derivatives, whose proton affinity is lower than that of olefins, preliminary ionisation is unimportant. It plays a major role in oxygen-containing solvents such as nitromethane, ethers, and carboxylic acids, whose proton affinities are comparable with those of olefins[165]. However, in this case the hypothesis of preliminary ionisation is inconsistent with the frequently observed second order of the reaction with respect to hydrogen chloride. If the rate of reaction were proportional to the concentration of the ions [Solv H^+] formed in the preliminary stage, defined by the expression

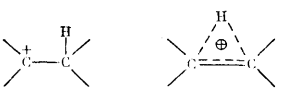
$$[Solv\,H^+] = \sqrt{K_{(HCl)_2}[HCl]^2[Solv]} = [HCl]\sqrt{K_{(HCl)_2}[Solv]} \ ,$$

subject to the condition [Solv H^+] $\ll$ [HCl], then the order of the reaction with respect to HCl should not exceed unity.

Thus the most probable pathway leading to the formation of ions in the reaction is the interaction of hydrogen chloride with the unsaturated compounds.

An ion pair can arise either directly on collision of the molecules or on decomposition of the complex of the unsaturated compound with one or several HCl molecules. These two pathways are kinetically indistinguishable. The enthalpies of formation of the complexes of HCl with olefins are much lower than the activation energy for hydrochlorination and complex formation does not therefore influence significantly the rate of ionisation.

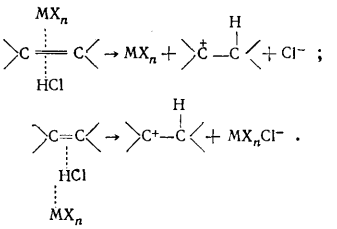
Ionisation results in the formation of an ion pair consisting of the carbonium ion and the HCl_2^- or Cl^- anion. These cations can have the classical (open-chain) or bridged structure:



Quantum-mechanical calculations indicate a greater stability of the bridged structure in the case of the $C_2H_5^+$ ion and approximately equal bond energies for the two structures of the vinyl cation $C_2H_3^+$.[163] In solutions the relative stabilities

of the two forms of the cations are determined by their solvation energies. Delocalisation of the charge diminishes this energy and for this reason in solution the stability of the ion with the classical structure increases. This structure of the carbonium ion is indicated by the high yield of the products of *cis*-addition in many hydrochlorination processes.

In the presence of a catalyst the transition state contains at least three molecules. Their interaction can occur in the following ways:



In the second case the formation of an ion pair is facilitated by the interaction of the catalyst MX_n with the anion Cl^- and this pathway appears to be the most probable.

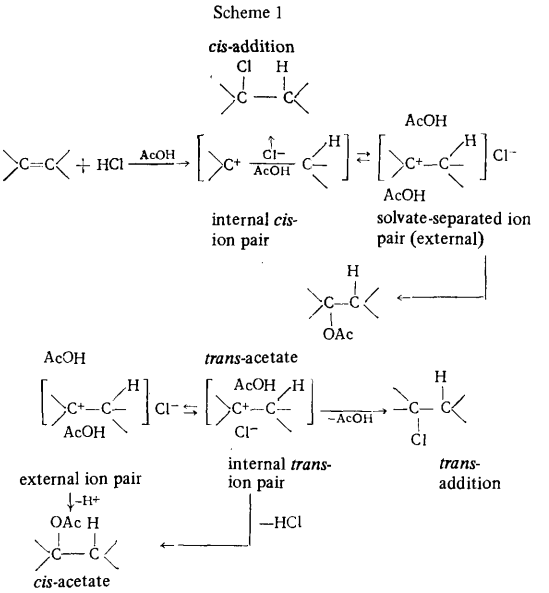
The formation of a stable complex of the olefin with the catalyst should not promote hydrochlorination. Indeed, the binding of $AlCl_3$ in a complex with an excess of the olefin inhibits the hydrochlorination and gives rise to side processes[103,104]. However, in the hydrochlorination of acetylene the catalytic activity of metal halides is correlated with the stabilities of the corresponding complexes of acetylene, which is due to the formation of ternary complexes[167]. The involvement of such complexes in the process is consistent with the molecular mechanism of hydrochlorination and is considered below in Section V.

According to Velichko-Shkurchenko[104] and Flid[106], in catalytic hydrochlorination ionisation precedes the formation of the complex acids $HMCl_{n+1}$ and ternary complexes involving the olefin. In certain cases the kinetic data demonstrate the simultaneous involvement of two olefin molecules in the ionisation stage[106].

(c) *The reaction product formation stage.* The hydrochlorination products are apparently formed directly from the ion pair[2,69,72]. This claim is based on the high (up to 100%) yields of the *cis*-addition products. The involvement in the process of the free open-chain ion, where there is a possibility of hindered rotation, should lead to identical amounts of the *cis*- and *trans*-products, which happens for a number of hydrochlorination reactions in highly polar media. For the bridged cation, preferential *trans*-addition is to be expected. *cis*-Addition is possible only for the ion pair[168], which agrees with the thermodynamics of the dissociation process. In solvents with $\varepsilon < 15$, the dissociation of the ion pair into singly charged ions requires an expenditure of up to 200 kJ mol^{-1} of energy and this process should not take place to an appreciable extent in media of moderate polarity[169].

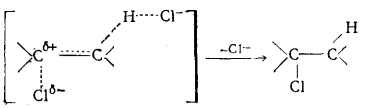
The conversion of ion pairs into reaction products can be considered within the framework of the competition between two mechanisms—the bimolecular Ad_{E^2} mechanism and the termolecular Ad_{E^3} mechanism[56,66,72,85]. The Ad_{E^2} mechanism describes the reaction of the ion pair obtained from the unsaturated compound and HCl. It is also applicable to a third-order reaction if the HCl_2^- anion is involved in it. The bimolecular process mechanism is presented below (Scheme 1) in relation to the interaction of the olefin with HCl in acetic acid[66]:

Scheme 1



Scheme 1 explains satisfactorily the formation of the *cis*- and *trans*-products of the addition of hydrogen chloride and the solvent. For 3,3-dimethylbutene, the ion pair is rapidly converted into the products; the ions external in relation to the ion pair cannot influence the formation of the products and the addition of salts and a change in the concentration of HCl do not affect their composition. The increase of the stability of the ion pair on passing to styrene increases the selectivity of the reaction: the ratio of the yields of the chloro-derivative and the acetate increases[56]. The Ad_{E^2} mechanism is characteristic of hydrochlorination at an insignificant concentration of the Cl^- anion; the occurrence of the reaction via this mechanism is promoted by an increase of temperature and the possibility of the delocalisation of the positive charge on the cation[85].

The termolecular mechanism is significant at high HCl concentrations or in the presence of additives of the type of $(CH_3)_4NCl$.[56,85,170] The transition state in Ad_{E^3} process can be represented as follows:



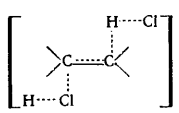
cis-Addition via this mechanism should be sterically hindered. The synchronous dissociation of the H–Cl bond and the formation of two new bonds and the delocalisation of the change in the transition state decrease the activation barrier to the reaction relative to the bimolecular process. A decrease of temperature promotes the occurrence of the reaction via the Ad_{E^3} mechanism. A similar Ad_{E^3} mechanism was first proposed for the addition of acids to acetylene derivatives in ionising media in the presence of LiCl as early as the 1950's.[171,172]

The presence of the Cl^- or HCl_2^- anions is of decisive importance in the termolecular process. The Ad_{E^3} mechanism explains satisfactorily the *trans*-stereospecificity of many hydrochlorination reactions under specific conditions. Addition via the Ad_{E^3} mechanism takes place in the absence of additives in the case of cyclohexene[71,170] and alkylacetylenes[85]. Highly polar and strongly ionising solvents tend to

increase the concentration of Cl^- anions and favour the Ad_{E^3} addition. The increase of the yield of the *trans*-product of hydrochlorination on passing from acetyl chloride to acetic acid and methanol is attributed to this[72]. The relative contributions of the bimolecular and termolecular mechanisms of ionic hydrochlorination depend on the choice of solvent and on the structure of the initial compound.

Thus the ionic mechanism of hydrochlorination with allowance for the competition between the Ad_{E^2} and Ad_{E^3} processes explains satisfactorily the characteristics of the reactions in strongly polar and hydroxylated solvents. Many characteristic features of the hydrochlorination in weakly polar media are inconsistent with the hypothesis of the involvement of ionic species in the reaction.

According to the ionic mechanism of addition in non-polar solvents of the type of pentane, the Ad_{E^2} pathway should operate with formation of the *cis*-hydrochlorination product. However, Table 2 shows that *trans*-addition is characteristic of many reactions in pentane. This is attributed to the fact that the hydrochlorination takes place by a synchronous mechanism with participation of two hydrogen chloride molecules via the transition state[70]



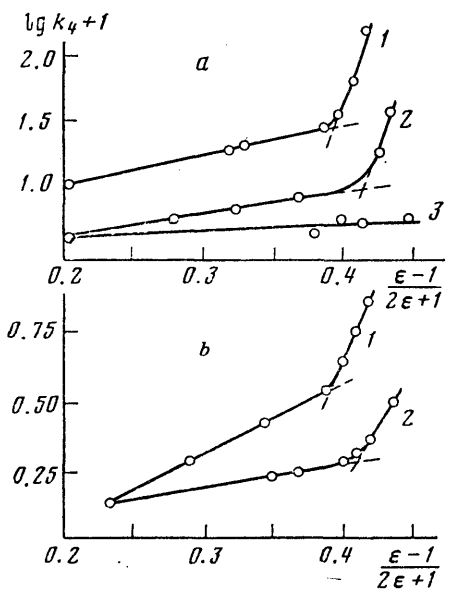


Figure 3. Dependence of the logarithm of the rate constant for the hydrochlorination of cyclohexene on the dielectric constant of the medium ε in terms of the Kirkwood variables at different temperatures (K): *1*) 293; *2*) 253; *3*) 183; *a*) C_6H_{14}–CH_2Cl_2; *b*) CCl_4–CH_2Cl_2.[6,109]

It is impossible to classify such a reaction as rigorously ionic, since the product is not formed via the ions but simultaneously with the formation of the latter. It has already been mentioned that the appearance of free ions in non-polar solvents requires a large expenditure of energy, while the hydrochlorination reaction in such media is characterised by a low activation energy. Thus it is not possible to account for the stereochemistry of the addition of hydrogen chloride in non-polar media from the standpoint of the ionic mechanism.

Nor does the ionic mechanism explain the fact that in many instances where the protonation of different olefins yields the same cation the products of the hydrochlorination of these olefins are different[46,93,173].

If the rate of the ionic process is limited by the ionisation stage, one must expect the acceleration of hydrochlorination on passing to polar solvents. In reality the increase of the rate of reaction with increasing polarity is frequently slight or does not occur at all. The ionic mechanism is not consistent with the kinetic isotope effect in the hydrochlorination of cyclohexene in hexane in the presence of $SnCl_4$.[110]

Estimation of the degree of charge separation in the transition state of the hydrochlorination reaction indicates the absence of ions from weakly polar media. For processes with a rate-limiting ionisation stage of the type of the solvolysis of alkyl halides and acid chloride or the Menshutkin reaction, the degree of charge separation $q^{\neq}$ is in the range 0.7–1.0 of an electronic charge unit[174]. Fig.3 illustrates the dependence of the rate of catalytic hydrochlorination of cyclohexene in terms of the Kirkwood variables on the polarity of the medium[6,109]. At temperatures in the range 253–293 K for media with dielectric constants below 6–8, $q^{\neq}$ is small and amounts to 0.2–0.4. At 183 K, $q^{\neq}$ does not exceed 0.3 over the entire range of dielectric constants $\varepsilon < 16$. The values $q^{\neq} \cong 0.5$–0.9, corresponding to an ionic reaction, have been obtained at 253–293 K in media of moderate polarity ($6 < \varepsilon < 12$).

Thus the ionic mechanism is unsuitable for the description of hydrochlorination in weakly polar media, particularly at low temperatures. The characteristic features of such reactions can be accounted for by a molecular mechanism, which is probable also for gas-phase processes where there are no solvation effects stabilising ions or ion pairs.

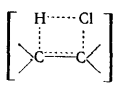
2. The Molecular Mechanism of Hydrochlorination

The molecular mechanism of hydrochlorination presupposes the formation of the addition product via a synchronous rearrangement of the bonds in the reactant molecules without their preliminary dissociation into ions or radicals. The energy consumed in the dissociation of old bonds is compensated by the energy of formation of new bonds. The synchronous rearrangement without dissociation takes place when the molecules in the transition state form a ring incorporating the carbon atoms of the double bond and one or several molecules of hydrogen chloride.

The energy of formation of the cyclic transition state from the molecules A and D is determined, according to modern ideas, primarily by the form of the potential curves for the ground and lowest excited configurations of the reacting system[175]. In those cases where the reactant molecules do not exhibit distinct electron-donating and electron-accepting properties, the excited configuration with charge transfer D^+A^- has a high energy and does not play a significant role in the formation of the transition state. Low activation energies may be observed if the ionisation potential I_D is relatively low and the electron affinity of the molecule A is high, i.e. under the conditions of a strong donor–acceptor interaction. In the reaction system considered, such interaction occurs, for example, on formation of complexes of

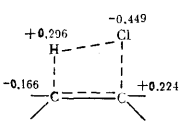
hydrogen chloride with unsaturated compounds. The formation of a cyclic transition state with a low energy in the HCl–olefin system is therefore possible. Four-membered and six-membered transition states are the most likely. The second and third orders of the reaction correspond to the four-membered and six-membered transition states respectively.

(a) *Second-order reactions with a four-membered transition state.* The addition to multiple bonds via a cyclic transition state of the type



has been considered in the literature before the appearance of the hypothesis that carbonium ions are involved in the reaction. Interest in such processes arose again after the publication of a study[14] in which the characteristics of the hydrohalogenation of olefins in the gas phase were accounted for by the involvement of the so called semi-ion pairs. In these pairs the reactant molecules are polarised and the charge on the hydrogen atom and one of the carbon atoms is +0.5, while that on the chlorine atom and the other carbon atom is −0.5. The energy of formation of ion pairs in the gas phase exceed significantly the observed activation energies for the addition reactions and the hypothesis of the polarisation of the molecules in the transition state and not their ionisation was therefore put forward. This hypothesis explained the validity of the Markovnikov rule and the correlation of the reactivities of olefins with their ionisation potentials. The choice of a charge of 0.5 is arbitrary, but calculation of the energies of formation of four-membered rings, where the molecules are polarised in this way, agrees satisfactorily with the activation energies for the gas-phase addition and elimination reactions. The proposed model agrees in the main with the results of semiempirical quantum-mechanical calculations[176].

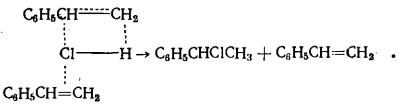
It has been suggested recently that the transition state be regarded as an asymmetric ring[177]. The quantum-mechanical calculation on the transition state in the ethylene–hydrogen chloride system by the INDO/3 method leads to a similar structure[128], for which the following charge distribution in the ring was obtained:



The asymmetric charge distribution leads to the large dipole moment $\mu^{\neq} = 2.88$ D. The overall charge on the HCl molecule is −0.153, which indicates charge transfer from ethylene to hydrogen chloride. The results obtained in the above study[128] agree better with the donor–acceptor properties of the reacting molecule than the hypotheses developed previously[14].

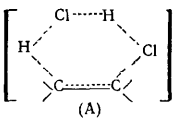
The agreement between the molecular mechanism of addition via a four-membered transition state and the orbital symmetry rules has been considered in a monograph[175] and in another publication[178]. It was shown that, in the presence of an appreciable charge transfer in the asymmetric transition state, molecular addition via a four-membered ring is possible.

The molecular mechanism with a four-membered transition state in the gas phase has been adequately proved. The possibility of a similar reaction in the liquid phase has been postulated[69,85], but so far this problem has not been analysed in detail and preference has been given to the traditional ionic mechanism. For the hydrochlorination of styrene, the following structure of the four-membered transition state, stabilised by a second styrene molecule, has been postulated[179]:



Although adequate confirmation of this mechanism has not been obtained, one cannot rule out the possibility of the stabilisation of cyclic structures by the molecules of olefins or other organic donors. For example, the characteristics of the hydrobromination reaction, which resembles the hydrochlorination process, in the absence of radical initiators can be explained, if it is assumed that the anomalous addition product is formed via a four-membered cyclic transition state stabilised by a second olefin molecule[5].

(b) *Higher-order reactions with a six-membered transition state.* The hydrochlorination products can be obtained via a synchronous rearrangement of the bonds in the six-membered ring formed by two molecules of hydrogen chloride and the double bond of the unsaturated compound:



(A)

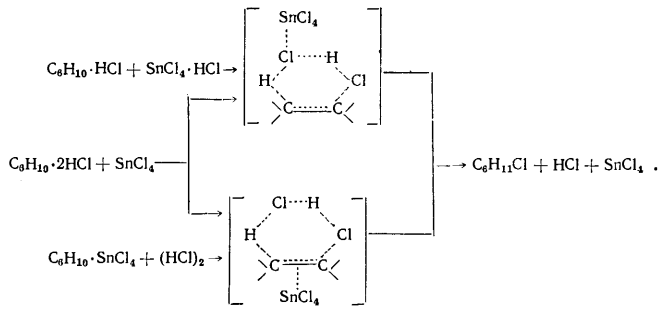
Addition via such a transition state has been demonstrated for the Diels–Alder reaction[180] and also for the exchange of atoms between the molecules of mixed halogens and their dimers[181] in the gas phase. This mechanism is most probable for bromination[182] and hydrobromination[5] in non-polar media. The above reactions are characterised by high negative activation entropies, low or negative activation energies, and a weak dependence of the rate of reaction on the polarity of the medium. The characteristics enumerated above are observed also in the hydrochlorination of many olefins in non-polar and weakly polar media. Large negative activation entropies are associated with the formation of highly oriented cyclic structures in which the gain in the free energy of activation is compensated by the decrease of the energy of the transition state as a result of the increase of the strength of the donor–acceptor bonds and the delocalisation of the electron density in the ring.

Six-membered cyclic transition states in hydrohalogenation were first proposed by Shilov to account for the *cis*-stereospecificity of the addition of HBr to acetylene derivatives[183]. According to the results of Smirnov-Zamkov and Piskovitina[184], the *trans*-addition of HBr to cyclohexene is also consistent with the molecular six-centre mechanism if account is taken of the steric disposition of the bonds in the cyclohexane molecule. The stereochemistry of the addition cannot serve as adequate evidence for or against the molecular mechanism. Our analysis[108] of the transition state in hydrochlorination reactions on molecular models showed that, under the conditions of a slight extension of the H–Cl bonds, a six-membered ring can be constructed for both *cis*- and *trans*-addition. The *trans*-pathway of the addition reaction does not therefore justify the rejection of the molecular mechanism as has been done by some investigators[75,168].

The formation of a six-membered transition state with a relatively low activation energy explains the finding that at room temperature HCl adds to olefins in the gas phase at a rate higher by many orders of magnitude than would follow from the extrapolation of the kinetic data for the high-temperature process[89]. The interaction of the transition state

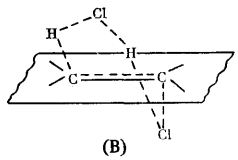
with a third hydrogen chloride molecule can lower the energy of the system. This mechanism appears to be the most likely for gas-phase reactions at room and reduced temperatures.

A molecular mechanism of a catalytic liquid-phase reaction has been proposed for the hydrochlorination of cyclohexene[6] in view of the low degree of charge separation in the transition state and the second order of the reaction with respect to hydrogen chloride. The reaction products can be formed via the following mechanism:



The transition states in the reactions have the same compositions but different structures and correspond to different stereochemistries of the addition. The nearly zero process activation energies in non-polar media at low temperatures and high (230–270 J mol^{-1} K^{-1}) negative activation energies as well as the appreciable isotope effect in the reaction of hexane are consistent with the molecular mechanism[6,108–110].

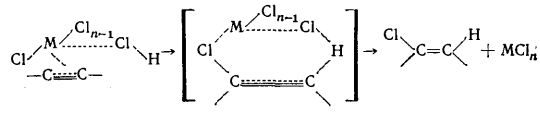
The orientation in the transition state is determined by the nature of the unsaturated compound. For the majority of olefins, the nearly planar structure (A) is more probable. Structure (B), which leads to the formation of the *trans*-addition product, may be more favourable for cyclic compounds:



(B)

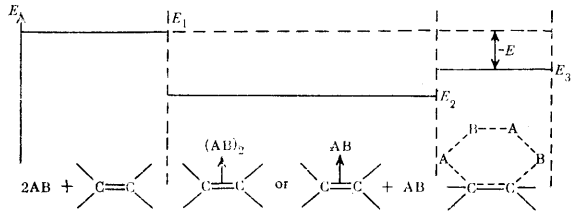
Lewis acids facilitate the reaction by stabilising the cyclic transition state. The catalyst can interact with a hydrogen chloride or olefin molecule. Both types of complex formation are accompanied by an energy gain; in the hydrochorination of cyclohexene in the presence of $SnCl_4$, the interaction of the catalyst with hydrogen chloride is more favourable.

Another six-membered transition state, incorporating in the ring the molecules of the unsaturated compound, hydrogen chloride, and the catalyst, has been proposed for the catalytic hydrochlorination of acetylenic derivatives[167]. The transition state of the process has a structure intermediate between a ternary complex of the starting materials and the reaction products:



This mechanism can be due to the ability of acetylenic compounds to form carbon–metal bonds and appears less likely for olefins. The absence of halogen exchange in the products of the hydrochlorination of cyclohexene in the presence of $SnBr_4$ at low temperatures rules out the formation of such a transition state[110]. At higher temperatures cyclohexyl bromide is formed in the reaction (after an inductive period). If the cyclic transition state incorporated a catalyst molecule, the bromide should have been obtained with a high yield simultaneously with the chloride, which has not been observed in a non-polar solvent.

High-order molecular reactions are characterised by low or negative activation energies E, which can be explained by the contribution of the heats of reversible intermediate stages, including complex formation[7], where the energy of formation of the cyclic transition state from the complexes is low and the energy level of this states lies below that of the initial molecules. The addition of the reactant AB to the double bond can be illustrated schematically in the following manner:



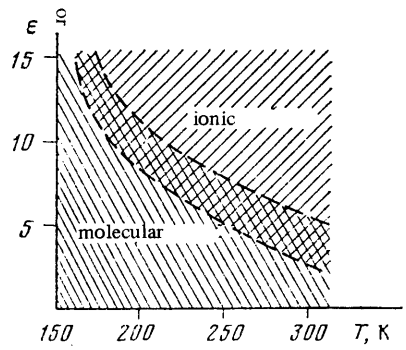


Figure 4. Schematic illustration of the preferential operation of different mechanisms of the hydrochlorination of cyclohexene in the presence of $SnCl_4$ as a function of the process conditions.

In this case E is determined by the expression $E = E_3 - E_1 < 0$. At high concentrations and low temperatures, the degree of binding in the complex is close to 100% and it is then to be expected that $E = E_3 - E_2 > 0$. A negative temperature coefficient, associated with the complex formation, is possible only when the complex lies on the reaction coordinate. If other causes of this phenomenon have been ruled out, then a negative activation energy serves as a criterion of the involvement of the complex in the process[7,182].

It is at present still difficult to formulate sufficiently unambiguous conditions for the occurrence of hydrochlorination via the molecular mechanism. The majority of the characteristic features of the processes in the gas phase and in non-polar solvents agree better with the molecular mechanism than with the ionic mechanism. The ionic mechanism has been demonstrated for reactions in highly polar and

hydroxylated media. In solvents with a moderate solvating capacity a transition from one mechanism to another is to be expected. A change in mechanism has been observed in the catalytic hydrochlorination of cyclohexene by noting the sharp breaks in the linear plots in terms of the Kirkwood variables (Fig.3) and has been confirmed by other data[6,110]. At room temperature the transition from the molecular to the ionic mechanism occurs even in the range of dielectric constants from 4 to 6. A decrease of temperature extends the region in which the molecular mechanism operates and at 183 K the majority of the features typical for the molecular pathway are observed even for $\varepsilon > 10$. Fig.4 illustrates the regions of the operation of the two mechanisms of the addition of hydrogen chloride in relation to the catalytic hydrochlorination of cyclohexene. Presumably the presence of substituents at the double bond stabilising the carbonium ion and also the introduction of Lewis acids stronger than $SnCl_4$ increase the region where the ionic mechanism operates.

The mechanism of hydrochlorination in frozen hydrogen chloride–olefin systems is of great interest. Reactive olefins such as isobutene react rapidly with hydrogen chloride below the melting point[12]. Presumably, as in the liquid phase, at low temperatures the solid-phase process takes place via the molecular mechanism.

* * *

The data on the product composition and the kinetics of the spontaneous and catalytic hydrochlorination show that the process proceeds via two mechanisms: ionic and molecular. Considerable activation energies and low activation entropies, a marked dependence of the reaction rate on the polarity of the medium, a high degree of charge separation in the transition state, the absence of an isotope effect in the reaction, and the formation of mixed addition products are characteristic of the ionic process. Zero or negative activation energies, high negative activation entropies, a weak dependence of the rate on the dielectric constant of the medium, the presence of an isotope effect, and the absence of mixed addition correspond to the molecular mechanism.

There is no reason to treat these mechanisms as mutually exclusive. They can operate simultaneously and have features in common. Thus ionisation can proceed via cyclic transition states characteristic of the molecular pathway and the energy expended on the formation of ions may be compensated by the energy of the C–H and C–Cl bonds formed. This mechanism may be called molecular-ionic. A molecular reaction without the participation of ions is characterised by a considerable charge separation. There apparently exist a whole series of intermediate cases between purely ionic and purely molecular reaction pathways.

The ideas which we have described differ from those in the scientific and monograph literature familiar to the majority of chemists. The new approach to the mechanism of the classical addition reaction became possible as a result of the development of kinetic studies, the application of modern experimental techniques, and the expansion of the range of experimental conditions. Further studies in this field will introduce additional revisions to the ideas being developed. The hydrochlorination reaction is not exceptional. The application of modern physicochemical methods in the study of the kinetics and intermolecular interactions, the expansion of the temperature and reactant concentration ranges, and the use of the results of quantum-mechanical calculations will undoubtedly lead to a significant revision of the traditional ideas concerning the mechanisms of many processes.

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The Determination of the Physicochemical and Chemical Forms of Trace Elements in Natural Waters

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Published material on methods for determining the physicochemical and chemical forms of trace elements (micro-elements) in natural waters in relation to their presence in definite water fractions (inorganic, organic, colloidal, surface-film, and suspended), magnitude, lability with respect to the analytical technique used, and the natural stability of their chemical compounds and oxidation state has been reviewed. All stages of the analysis, from the selection of the position for the removal of the samples and their preliminary treatment to the instrumental determination of the forms of the trace elements have been examined. The bibliography contains 175 references.

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I. INTRODUCTION

The degree of contamination of inland and coastal waters in many industrially developed countries now exceeds an ecologically safe level. The principal contaminants of natural waters (NW), in addition to pesticides and petroleum, are the trace elements (TE), with concentrations below 1 mg litre^{-1} water (1 p.p.m.), many of which are highly toxic—Hg, Pb, Cd, As, etc. Only in recent years has it been possible to obtain reliable values of the total concentrations of Te in various NW, which have proved to be at the level of several micrograms per litre, or in many cases tenths or hundredths of this figure.

The determination of the total concentration of TE, however, does not give definite information on the toxicity of water, since there is no direct relationship between these parameters. A knowledge of the forms in which TE exist in NW has therefore become of primary importance, since in addition to different biological accessibility[1] they have a significant influence on the geochemical cycles and the transfer of TE in NW, the methods of obtaining domestic water and water for industry, etc.

There are two basic approaches to the study of the forms of TE in NW. The first of these is theoretical, and calculates the equilibrium concentrations of all dissolved forms by means of mathematical models based on the use of the experimentally determined concentrations of TE and ligands, and also the published values of TE–ligand stability constants. Chemical modelling now covers all competing equilibria, and computer programs are used for thermodynamic calculations. The accuracy of computer modelling is lowered considerably, however, by variations in published data on stability constants and activity coefficients. Moreover, the calculation generally does not include many of the parameters influencing the form of TE, since qualitative and quantitative data are not available for many of them: pH, redox potential, the great majority of organic ligands, colloidal particles and adsorption on them, inter-phase reactions of precipitation, solution, and sorption, biological and physical processes, etc. These factors, and also the lack of information on the non-equilibrium conditions existing in many NW, cast doubt on the relation to reality of the results of the calculation of the forms of TE. Chemical modelling has been described in detail elsewhere[2-9].

The second approach to the study of the forms is analytical. It is convenient to divide all experimentally determined forms of any TE in NW into two large groups: 1) the physicochemical forms present in definite fractions of NW (for example, dissolved organic and suspended), which are subdivided either according to size (for example by ultrafiltration and gel filtration) or their lability with respect to the analytical technique used (for example, ion exchange and stripping voltammetry); 2) the chemical forms, characterised either by definite chemical compounds (for example, MeHgCl and Ph_4Sn) or by a definite oxidation state in different classes of TE (for example, inorganic Se^{IV} and Se^{VI}). According to this classification, the chemical forms of TE represent a fraction of their physicochemical forms, which in sum give the total concentration of TE in NW.

At the very low concentrations of TE in NW, the determination of their forms has proved to be an extremely difficult analytical problem, which has not yet been solved. The forms of TE are very sensitive to large variations in salt composition, pH, the concentration of dissolved organic and macromolecular compounds, colloidal and suspended particles, etc., which also depend on the type of NW and the time of year[10]. The equilibrium concentrations of the forms of TE present in NW are unavoidably changed on the removal of samples, as a consequence of their contact with oxygen and with the walls of the sampling equipment, changes in temperature and pressure, and the methods of separation (isolation) and analysis used. The extent of these changes is not known, but it is important to reduce all these effects to a minimum.

The aim of the present work is to summarise methods for determining the physicochemical and chemical forms of TE in NW in the last 5–7 years. The former have been reviewed[2,11,12], and their development followed[7], while the latter have been partly reviewed, but only for sea water[13]; in recent years, however, new experimental results have extended considerably existing views on the physicochemical and chemical behaviour of TE.

Since most errors in the determination of the concentration of TE and their forms in NW due to the introduction of contaminants are made during the removal and preliminary treatment of specimens for analysis, these stages will be examined, and recommendations given for carrying them out correctly. Colloidal particles which pass through a filter with a pore

diameter of 0.45 μm will be assigned to the dissolved fraction, although they introduce some ambiguity into the definition of the colloidal and dissolved forms of the elements.

The analytical methods most frequently used for determining the forms of TE are stripping voltammetry (SV) (its use for NW has been reviewed[14]), atomic-absorption spectrophotometry (AAS), emission spectrometry (ES), gas–liquid chromatography (GLC), neutron-activation analysis (NAA), mass spectrometry (MS), liquid chromatography (LC), and spectrophotometry. The last method will not be considered, however, because of its low selectivity and the consequent impossibility of taking correct account of the interfering influence of many other TE and chemical substances present in NW.

II. THE REMOVAL AND STORAGE OF NATURAL WATER SAMPLES

The reliable determination of the concentration of TE and their forms in NW is possible only when contamination is excluded at all stages of the analysis: in the laboratory on shore when containers are being washed for an expedition, in the removal of samples and their filtration on board the vessel, during their conservation and storage, and also during the measurement using the instrument. All these stages must be checked for the possible introduction of contaminants, since attempts to achieve high purity at any one stage may be nullified by contamination at another stage. It is therefore recommended[15] that specimens be treated both on board the vessel and in the laboratory on shore in so-called "clean" rooms with dust-free air, in which there are no metal surfaces, and the work is carried out in special clothing in an extraction cupboard. It is difficult to observe all these requirements, but an essential condition is the absence of dust, which is achieved by working in a clean extraction cupboard. The preparation of ultrapure water for trace analysis has been described[16].

Experience has shown that the most vulnerable stages of the analysis to the introduction of contaminants are the collection, filtration, and storage of the samples.

a) Sample Collection

The choice of position is important only for surface specimens. The chief danger is possible contamination of the water surface by the vessel. Samples of all types of NW should therefore be taken at a distance from the vessel, either from a ship's boat[15] or from a rubber boat at its moving front in uncontaminated water from the windward side[17]. This method cannot be used, however, when there are waves or when a large number of specimens is required.

The procedure for collecting samples is now well developed[17–20]. Samples are collected using bottles, sampling devices, and suction systems. The best materials for these are Teflon, polycarbonate, polypropylene, and polyethylene. Various types and their characteristics were recently described[15] and compared in the removal of identical samples[16]. Unfortunately, they all show unsatisfactory features. Thus bottles and suction assemblies are suitable only for the collection of relatively shallow specimens, whereas the widely-used Niskin and Go-Flow deep-water sampling devices are open when they pass through the surface layer and are often made of polyvinyl chloride, which is usually contaminated by TE. Sampling device designs free from these unsatisfactory features have now been developed, however[15].

b) Filtration

When the forms of TE have to be determined, it is necessary to filter the specimen as soon as possible after collection, through a membrane filter with a pore size of 0.45 μm, since the distribution of the forms of TE in unfiltered water may change rapidly, mainly as a consequence of bacterial activity and, to a lesser extent, adsorption–desorption processes. If the time required is greater than several hours, the sample must be cooled to ~4 °C before filtration is complete. All phytoplankton and most bacteria remain with the suspended matter on the filter[19]. Filtration is particularly important for fresh water and estuarine water, in which the suspended form makes up a significant fraction of the total concentration of an element. By general agreement[21], the filtrate contains the dissolved fraction of TE, which, however, also contains colloidal particles and a fraction consisting of very fine particles of mineral and biological origin which pass through the filter[22].

Polycarbonate or cellulose acetate Nuclepore, Millipore, Gelman, and Synpore filters are generally used; these must be purified from TE before use by washing thoroughly with mineral acid, distilled water, and the sample[2,19,22,23]. The absence of clean conditions in the determination of TE has been discussed[24]. The separation of the phases is carried out in a vacuum, under pressure, and by centrifuging. Their advantages and disadvantages, and types of filtration apparatus, have been described[19].

c) Storage

It is often impossible to analyse samples for TE immediately after collection and filtration. It then becomes necessary to store them before analysis. Here the main problems are adsorption losses, which depend on the storage time[25], and contamination[19,26,27]. Sorption depends chiefly on the TE concentration, the material of the storage vessel, pH, and salinity[27]. NW samples must be kept in vessels of Pyrex glass, Teflon, or high-density polypropylene or polyethylene. Wash solutions, consisting chiefly of a mineral acid[28], have been proposed for cleaning them, and the treatment conditions are generally different. It is not possible to compare their efficiency for different NW, vessel materials, and storage conditions, however, because of the inadequate experimental conditions. This comparison has been made only for the storage of fresh water in polyethylene vessels at 1 °C;[28] it was found that it is best to clean the vessels by shaking with 10% HNO_3 for 48 h. It has also been suggested that vessels for the storage of all types of NW should be cleaned by shaking with 2 M HCl and then washing with a filtered sample[19], since acid washing removes surface contamination from the walls of the vessels, but at the same time activates adsorption centres capable of removing TE from the sample.

To ensure minimum adsorption losses during the storage of samples in which it is necessary to determine only the total concentration of TE, the samples after filtration are usually acidified with HCl or HNO_3 to pH $\leq$ 2.[19,20,26] In the case of germanium, for example, they can be kept for several years[29]. In the determination of the physicochemical forms of TE, however, acids cannot be added. When filtered samples are stored at natural pH and room temperature, bacterial activity leads to the appearance of suspended particles and a decrease in the concentration of organic substances and hence to either the removal of TE from the solution or a change in their forms[19]. Thus to decrease bacterial activity and hence the loss of TE, it is suggested

that NW samples be kept in a refrigerator at 4 °C [30] for up to 1–3 months[31–33]. For the same purpose, sea water samples are kept in the frozen state between −20 °C and −45 °C, for up to three months without treatment[34], after filtration[22,32], and after filtration and acidification[22,35]. In the case of fresh water, a decrease in the labile form of TE has been observed[33].

The storage of samples for the determination of the total concentration of mercury shows differences, however, related to the characteristic features of its chemical and physical properties. Firstly, they cannot be kept in polyethylene vessels, whose walls are permeable to mercury vapour[36–38], but only in glass vessels. Secondly, Hg^{II} is readily sorbed on the walls and reduced to Hg_2^{II}, followed by disproportionation to Hg^0. In sea water, these processes are suppressed by acidifying with mineral acids[37], and in fresh water and dilute standard solutions by the further addition of oxidising agents, for example $K_2Cr_2O_7$ to a concentration of 0.05%,[36,39,40] or complex-forming agents, for example NaCl to a concentration of 3–4%.[37,41] Under these conditions, specimens and standard solutions can be kept for several months.

There are no general methods, however, for the storage of samples for the subsequent determination of the chemical forms of TE, in contrast to the case of their physicochemical forms. These are usually found empirically. Samples with inorganic forms of As^{III} and As^{V} can be kept for three weeks at room temperature[42], 10 days at ~4 °C,[43] for a long time below −15 °C,[44,45] for several days when acifified to 0.05 M HCl,[46] and for 125 days at pH 1.5.[47] In the case of inorganic forms of Se^{IV} and Se^{VI}, samples can be kept for a long time at 4 °C,[48] in the frozen state[49], or when acidified[49,50], for 125 days at pH 1.5,[48] and for 4.5 months at pH 2.[51] Different storage conditions of pH, concentration, and type and size of storage vessel material have been studied for the storage of As^{III}, As^{V},[36] Se^{IV} and Se^{VI}.[48] Samples containing methylarsinic acid (MAA) and dimethylarsinic acid (DMAA) can be kept indefinitely when acidified to 0.05 M HCl.[44] The vessels must be sealed to exclude atomospheric oxygen.

Very little is known about the storage of samples with chemical forms of other TE. Thus $MeHg^{II}$ can be kept for not more than 10 days at pH 2.5,[38] but it is lost quantitatively on lyophilisation[52], and Ph_2Hg and RHg^{II} (R = Me, Et, Ph) are only slightly converted to Hg^{II} after 30 days in 1% H_2SO_4.[40] It has also been noted that little Cr^{VI} is lost at pH 6–8,[53] but R_4Pb cannot be stored at all[54], since in river water it decomposes to the extent of 60% in 24 h.[55]

III. PHYSICOCHEMICAL FORMS

For most TE determined, stripping voltammetry (SV) has low detection limits, which for the most part coincide with their average concentrations in NW, and does not require preliminary chemical preparation of the samples. Thus combined with various methods of separation and decomposition it has been made the basis of recently developed general schemes for determining the physicochemical forms of trace metals (TM).

In the first of these[2,56,57], the following are measured in the sample after filtration through a membrane filter with a pore size of 0.45 μm: a) SV-labile metal, and b) total metal. The determinations are carried out systematically: 1) before treatment of the sample; 2) after it has passed through a column of Chelex-100 ion exchange resin; 3) after ultraviolet irradiation; and 4) after passage of the photo-oxidised specimen through a column of resin. This makes it possible to separate the physicochemical forms of the TM into the four classes given below, of which the last three are further divided into inorganic and organic forms, so that it is possible to determine seven dissolved forms of each metal: 1) free metal ions and labile complexes (in sea water at natural pH, this form corresponds to simple inorganic complexes such as chlorides and sulphates, and in fresh water to citrate and aminoacid complexes); colloidal metals; 2) SV-active and 3) SV-inactive (these classes in sea water correspond chiefly to metals adsorbed on organic and inorganic colloidal particles, or included in them, since the presence of appreciable concentrations of metal complexes which would not be held by the resin is unlikely; in fresh water the picture may be different, because of the higher concentrations of organic substances, particularly such powerful complex-forming agents as humic and fulvic acids; 4) labile complexes which dissociate on passage through the resin, for example those with cysteine, and also dissolved sulphides and silicates. There are no strict boundaries between these classes, however, and there is some overlap. An important advantage of the scheme is the low reagent background[58]. The dependence of the possible physicochemical forms of metals on their size is given in Table 1.

Table 1. Possible physicochemical forms of TE in NW in relation to their dimensions[2].

Form	Example	Approximate dimensions (μm)
Suspended	remains on a filter with pore diameter 0.45 μm	>0.45
Simple hydrated metal ions	$(H_2O)_6Zn(II)$	0.0008
Simple hydrated complexes	$(H_2O)_5ClZn(II)$	0.001
Simple organic complexes	Cu glycinate	0.001—0.002
Stable inorganic compounds	PbS, $ZnCO_3$	0.001—0.002
Stable organic compounds	Cu fulvate	0.002—0.004
Adsorbed on inorganic colloids	Cd(II)—MnO_2 Cu(II)—Fe_2O_3	0.01—0.50
Adsorbed on organic colloids	Pb(II) -humic acid; Zn(II) -organic detritus	0.01—0.50

Note: In this and subsequent tables M(II) = M^{II}, M(III) = M^{III}, etc.

The use of this scheme has shown that in coastal sea water[32], up to 40–60% Cu, 45–70% Pb, and 15–35% Cd, relative to their total concentrations, are combined with colloidal particles; in fresh water[33], Cu also predominates in these forms, but Pb is present in suspended inorganic form, and Cd exists only in labile ionic forms.

The results obtained using this scheme, however, do not necessarily reflect the true equilibrium concentrations of the forms of TM, because of their decomposition when an acid, the acetate anion, or a mercury salt are added to the sample being analysed[59,60].

Another general scheme for fresh water[61] is based on the fractionation according to the dimensions of the forms bearing the metals by filtering the samples through membrane filters with pore sizes of 12 μm and 1.0 μm, followed by ultrafiltration of the last filtrate through filters with pore sizes of 0.4, 0.08, and 0.015 μm (it is possible to divide the forms into even finer fractions by ultrafiltration through filters with pore sizes of 0.014, ~0.005, and ~0.0012 μm, but it has been found that ultrafilters do not have absolute pore sizes and

show variable adsorption, so that it has not been possible to obtain consistent results). The last six fractions are analysed for the total metal concentration by SV after photo-oxidation (Cd, Pb, and Cu) and by flameless AAS (Fe and Mn). In the series of filtrates, SV-labile metals are found at natural pH before and after ultraviolet irradiation. Particular attention has been paid to the limitations of the different schemes, and it has been shown that photo-oxidation is not suitable for the quantitative estimation of the forms in fresh water.

The continuum of the dimensions of the forms in this scheme makes it possible to avoid an arbitrary distinction between dissolved and suspended metal, and also emphasises the importance of colloidal fractions of the metals. The scheme has been used for fresh water[61,62]. In particular, it has been shown that the difference in the forms of metals in the waters of two rivers is due to a marked difference in the concentration of suspension, and that only a small fraction of the metals is SV- and Chelex-100-labile. The results[61] have also revealed a marked lack of agreement with the physico-chemical model for TM in fresh water[63], due to the inability of the latter to take account of suspended and colloidal forms of the metals.

Another approach to the continuum of dimensions of dissolved form of TM in fresh waters[64] is based on the principle of successive ultracentrifuging[65]. The sample is first filtered through a filter with a pore size of 0.45 μm, and then fractionated successively according to molecular mass through ultrafilters with pore sizes of 100 K, 25 K, 10 K, and 1 K (where K is the molar mass in multiples of 1000); this makes it possible to divide the dissolved organic matter and the forms of TM into definite fractions, depending on their molecular masses. In each of the fractions obtained, the metals are determined by SV and AAS. The highest concentrations of Cd, Pb, and Cu are found in fractions with molecular mass 10^3–10^4, and correlate with the concentration of organic carbon; there are no free or labile forms present. On the other hand, Fe and Mn are often found in fractions with higher molecular mass, and do not correlate with the concentration of dissolved carbon, and Ca and Mg are bound in fractions with lower molecular mass. The same regular features were observed for Cu by ultrafiltration and gel filtration[66].

A combination of a large number of analytical methods[12] can be used to determine the following forms of TM in fresh water: total, suspended, dissolved, free ionic, and combined, and also the distribution of the complexes with respect to molecular (ionic) mass in the range ~500–150000. Its advantages include the possibility of finding the sign of the charge of the free and complexed metal ions and studying complex formation, including its kinetics. Dissolved Mn is present chiefly as anionic complexes with high molecular mass. A serious disadvantage of the scheme is the insufficient attention to colloidal forms.

These general schemes cannot be used in many laboratories, however, because they are relatively complex and laborious. Simplified schemes for determining the physicochemical forms of TM, or individual fragments of general schemes, or details of the latter, have therefore been widely used.

In one simplified scheme[67,68], Cd, Cu, Pb, and Zn are determined in the suspended and dissolved forms, and in the latter the ion-exchangeable (free metal ions and simple inorganic and organic complexes) and combined (mainly a colloidal fraction with molecular mass less than 1000) forms. It has been applied to fresh and estuarine waters[69].

In another scheme[34], the sample is first filtered through a filter with a pore size of 0.22 μm to remove micro-organisms, after which part of the filtrate is passed through a filter with a pore size of ~0.001 μm with a restricted nominal molecular mass of 1000 to separate the forms with high and low molecular masses, that is colloidal and true dissolved forms. The three fractions obtained are analysed for the concentrations of total metal, the SV-labile forms at natural pH, and the SV-acid-labile forms at pH 2.8 (in the last case except the original specimen). This scheme has shown that in sea water, Cd is present exclusively in labile forms of low molecular mass, and Pb chiefly in non-labile forms of low molecular mass, while the distribution of Cu was irregular, with appreciable binding in colloidal and organic forms.

The range of experimentally determined physicochemical forms of TM is not restricted to the above schemes. To improve understanding of the role of TM in NW, it is necessary to have finer sub-divisions within each form or fraction. Thus depending on the time of contact with Ca-Chelex-100 resin, SV makes it possible to define the relative lability of TM as very labile, moderately labile, and inert[70,71]. This kinetically based classification may be useful for estimating the bio-availability of TM. In particular, Cd and Zn exist in forms more labile than Cu and Pb.

Identification of the lability of TM with their bio-availability may lead to serious errors, however, since the measured concentrations of labile metals depend markedly on the analytical conditions and the method used—SV, ion exchange, solvent extraction, absorption, etc. In particular, in SV the labile forms are free metal ions, together with metal complexes, which will dissociate in the diffuse layer, liberating the metal ion. The possibility of a more exact treatment of this term from the viewpoint of the values of the equilibrium and rate constants has been discussed[7]. For example, this method has shown[72] that in sea water, with decrease in pH from 8.1 to 2.0, there is a sharp increase in the proportion of labile Cd, Pb, and Cu detected: 0.17 → 0.45, 0.34 → 1.91, and 0.67 → 2.43 μg litre^{-1} respectively. When they are concentrated on Chelex-100 resin at pH 1 with subsequent determination by the same method, however, the Cd, Pd, and Cu concentrations obtained were 0.31, 0.81, and 2.03 μg litre^{-1} respectively. An increase in the labile fraction of TM when the samples were acidified has been observed by other workers[73]. This can be attributed to the conversion of colloidal, acid-sensitive, and acid-exchangeable forms into labile forms. Labile mercury is defined as that fraction in NW which is reduced by $SnCl_2$.[74–76]

The labile fractions of TM usually make up only a small proportion of their total concentration in NW. Most of the TM are combined with organic, colloidal, and suspended fractions, particularly in fresh, estuarine, and coastal sea water. The first of these fractions may contain an appreciable and even a greater proportion of TM, both in fresh water: Cu,[31,33,77] Cd,[78,79] Al, Cr, Fe, Pb,[80] and Hg;[78,81] and in sea water: Cu,[73,82,83] Zn,[73,83], Pb,[73] and Hg.[74,84]

Organic forms of TM are separated from the sample on anion-exchange resins[77,83], and organic mercury together with inorganic mercury on resin[85] and polyurethane[86] treated with dithiocarbamate, or on silica gel covered with benzothiazole-2-thiol.[87] They can be fractionated according to molecular mass or size by ultrafiltration[78,84,88], centrifuging[79,88], ion-exchange membranes[88], gel chromatography[80], and gel filtration[89,90]. The organic fraction of TM can be found less accurately from the difference between the total and labile metal in the same sample, determined by the same method. For this purpose it is necessary to separate the TM from their organic complexes and compounds, and also their colloidal particles. This is achieved by boiling the sample at pH 0.7 [58] or by ultraviolet irradiation[31,82,91,92]. The last method, involving irradiation by a 550 W mercury

lamp for 4 h, is particularly noteworthy, since it is suitable for all types of NW and gives a low reagent background[92]. In the determination of total Hg, because of the fairly high stability of its organic derivatives, the latter are decomposed by ultraviolet irradiation[91,93], or oxidising agents such as $K_2S_2O_8$, $KMnO_4$, Br_2,[37,39,74,94] or reducing agents such as $NaBH_4$,[95] $SnCl_2$ and $CdCl_2$, after concentrating the Hg on a resin treated with dithiocarbamate[96], or by combustion of the resin with the Hg at 850 °C.[85]

The important role in the binding of TM of colloidal particles of inorganic (hydrated oxides of Fe, Mn, Si, clays, and sulphides) and organic (humic substances, biota residues) origin has been emphasised[2,58]. Metals present in ionic forms and combined with colloidal particles are separated by dialysis, ultrafiltration, centrifuging, ion exchange, and electrophoresis, the methodology of which, together with methods of determining colloidal forms of TM, is given in the above schemes (see also Refs.2, 58, and 82). In particular, the concentration of more than 30 metals in colloids can be determined by NAA after ultrafiltration of the sample through a filter with a pore size of 0.0012 μm.[97] Cation exchange resins apparently do not concentrate colloidal forms of TM at natural pH,[58] which are too large to enter the pores of the resin. An important feature is that it is often difficult to prove unambiguously whether TM are present in the colloidal, particularly organic, fraction or in the dissolved organic fraction, if they are not clearly separated from one another. Thus the extent of the distribution of the TM between them is often only tentatively determined.

Most NW show coordinative unsaturation, revealed by the binding of added ionic TM. It is assumed that this so-called complex-forming power of NW is due to the presence of organic substances of the fulvic acid type. Analytical methods for determining it (amperometric titration, ion-selective electrodes, ion-exchange equilibria, etc.) and the theoretical basis of the concept have been reviewed[98].

Suspended particles play an important role in the distribution of TM in NW. Thus rivers may carry most of them (up to 80–90%) to the ocean in suspended form[83,99]. Mercury may also be present chiefly in this form in estuarine[100] and sea[101] water. The concentration of TM in the suspension may vary considerably, however, depending on the time of year[102].

Usually, suspended fractions of TM are separated from dissolved fractions by three methods—filtration, centrifuging, and precipitation[103]—but most frequently the suspension is removed on membrane filters with a pore size of 0.45 μm. The concentration of TM in the suspension remaining on the filter can be determined by several methods, depending on the availability of methods for treating the suspension and on available analytical methods. A number of the latter (NAA and ES) make it possible to determine many TM simultaneously without any treatment of the suspension[104,105]. Combustion of part of the filtrate with the suspension in an atomiser has been proposed for the determination by flameless AAS of a number of metals having approximately equal volatilities[106].

In most cases, before determination, the TM together with the filters are transferred to solution either with complete solution of the suspension or with extraction using acids without affecting the crystal lattices of the suspension. In the first case, a necessary component of the decomposition mixture is hydrofluoric acid, together with various other mineral acids[107–109]. It can also be achieved by fusing the suspension at 1000 °C with $LiBO_2$ with subsequent solution in HNO_3.[109] The extraction is usually carried out either by heating the suspension with mineral acids under different conditions[109–113] or with their mixtures[101,114], or with acid and 30% H_2O_2,[85] or by combustion of the suspension in a furnace at 450–600 °C followed by solution in HCl.[115,116] The TM in the solutions obtained are most frequently determined by AAS.

Suspended TM are sometimes found from the difference between their concentrations in the unfiltered and filtered samples[100,117]. Dispersion of the suspension in an ultrasonic bath after solution of the filter in $CHCl_3$, with subsequent determination by flameless AAS, has also been described[118].

In addition to the two phase forms of TM, dissolved and suspended, MW also contain a third form, the film (surface micro-layer), which contains the highest concentrations in NW of dissolved and suspended TM, and also organic substances, biogenic elements, etc. Compared with the layer under the water surface, the concentrations of dissolved TM may be several times greater[117], and the concentrations of suspended TM greater by a factor of up to 10, in fresh[117] and sea[114] water. The organic and inorganic forms of TM can be determined in the suspended film fraction[119]. Usually, the surface film of thickness <0.3 mm is removed, by various methods[120], including sampling devices[121].

Of the analytical methods for determining the dissolved physicochemical forms of TM without preliminary separation from the sample, only SV is used, because of its high sensitivity and simplicity of operation, and also the availability of instruments and equipment. Its use to determine the forms of metals has been described in detail[2,122]. The main limitation of SV is that it is applicable to only a small number of TM—Cd, Pb, Cu, and Zn. In recent years, the development of polarographic methods has made it possible to obtain information on the chemical state of a number of other elements—Tl, Cr, Sb, As, Bi, and U.[2,7]

The use of other analytical methods involves the preliminary concentration of the TM, which can be achieved by various methods[123], including filtration of the sample through chelating filters[124]. Methods of concentration have been compared[125,126]. All the stages in the analysis of TM in NW have been described in detail for the following methods: AAS,[20,126–128] NAA,[129] ES,[130] and X-ray fluorescence[131].

IV. CHEMICAL FORMS

Because of the extremely low concentrations of the chemical forms of TE in NW, only a few examples of their determination without concentration have been described. The determination of Cr^{III} by a chemiluminescent method with a detection limit of 0.02 μg litre^{-1} has been proposed[132]. As^{III} can be determined by differential pulse polarography (DPP) with a detection limit of ~10 μg litre^{-1},[46] but As^{V} is found from the difference between As (total inorganic) and As^{III} after reductive evaporation of the sample, with a detection limit of ~1 μg litre^{-1}. Hg^{II}, $MeHg^{II}$, and $PhHg^{II}$ have been determined separately by AAS in an automatic system on the basis of the selective reduction of combinations of these forms by EDTA, $SnCl_2$, and $CdCl_2$. The low detection limit of ~0.001 μg litre^{-1} was obtained as a result of the equilibrium of mercury vapour with a small volume of air at 90 °C.[40]

Because of the insufficient sensitivity of present-day analytical methods, the determination of most chemical forms of TE requires concentration, which can be achieved using liquid extraction, solid extracting agents, and the formation of volatile hydrides.

Methods for determining the chemical forms of TE with concentration by liquid extraction are given in Table 2. Inert compounds, for example R_4Pb, are extracted by

organic solvents such as hexane or benzene. After separation by GLC, the forms are determined by AAS with a detection limit of 0.2–0.5 μg litre^{-1}.[54,55] Most chemically active forms of TE must be concentrated by extraction with organic solvents in the presence of complex-forming agents. For Bu_nSn^{IV} (n = 1–3), tropolone is used. The forms in the extracts are alkylated by Grignard reagents to the corresponding methyl[133] and pentyl[134] derivatives of tin, and the latter are analysed. $MeHg^{II}$ and $PhHg^{II}$ are concentrated using dithizone, and RA makes it possible to determine them with a detection limit of 0.01 μg litre^{-1}.[135] Se^{IV} can be determined with detection limits of 0.0008 μg litre^{-1} and 0.002 μg litre^{-1} using 4-nitro-o-phenylenediamine[51] and 1,2-diamino-3,5-dibromobenzene[137] respectively. By oxidising $Se^{-II,0}$ with bromine and reducing Se^{VI} with a mixture of bromine and bromide to Se^{IV} with the last ligand, it is possible to determine all these forms separately. Their distributions in river and sea water have been given[138].

Table 2. Methods for determining the chemical forms of TE with concentration by liquid extraction.

Chemical form of TE	Extraction	Method of determination	Refs.
R_4Pb (R=Me, Et)	hexane	GLC-AAS	[55]
Me_nEt_mPb (n=m=0–4)	ditto	ditto	[54]
Bu_nSn(IV) (n=1–3)	tropolone	GLC-MS	[133]
ditto	ditto	GLC	[134]
MeHg(II), PhHg(II)	dithizone	RA*	[135]
Hg(II)	mixture of amines	GLC	[136]
MeHgCl	4-nitro-o-phenylenediamine	ditto	[51]
Se(IV)	1,2-diamino-3,5-dibromobenzene	»	[137]
ditto	ditto	»	[138]
Se (—II; 0) Se(IV), Se(VI)	ammonium salt and thiocyanate	AAC	[53]
Cr (III), Cr (VI)	dithiocarbamate	AAS	[139]
As (III), As (V)	ditto	RA	[140]
ditto		AAS	[141]
»	»	ditto	[142]
As (III), As (V) Sb (III), Sb (V) Se(IV), Se(VI)			
Sb (III), Sb (V)	»	»	[143]
Se (IV), Se (VI)	»	»	[144]
Te (IV), Te (VI)	»	»	[145]
Cr (III), Cr (VI)	»	»	[146]
Cr (VI)	»	»	[147]

*RA = radioanalytically.

In a similar method, As^{III} is first determined using dithiophosphate (detection limit 0.006 μg litre^{-1}), and then As^V is determined after reducing to As^{III} using sulphite[139].

Pyrrolidine- and diethyldithiocarbamates are used particularly frequently as complex-forming reagents. They have been used for the selective extraction of As^{III},[140–142] Sb^{III},[142,143] Se^{IV},[142,144] Te^{IV},[145] Cr^{VI}.[146,147] The interfering influence of many metal ions is masked by adding EDTA.[141,143–145] The total concentration of these elements is then found by using KI [140,141] with acidification[143], heating[146], or boiling[144,145] with acids to convert all the inorganic forms of these elements into the above forms, and, from the difference between them, the forms As^V, Sb^V, Se^{VI}, Te^{VI}, and Cr^{III}. The detection limit is 0.2 to 0.4 μg litre^{-1} [140,141,143–145] or 0.02 μg litre^{-1}.[147] In NW, the highly oxidised forms of these elements predominate.

The use of GLC to determine organomercury compounds and inorganic mercury compounds by converting them into organic compounds has been reviewed[148]. LC has been used for the quantitative separation of RHg^{II} (R = Me, Et, Ph), R_3Pb^{IV} (R = Me, Et), and $MePh_3Sb^V$,[149] organic derivatives of Hg, Sn, Pb, and As,[150] and metal ions[151].

Methods for determining the chemical forms of TE with concentration on solid extracting agents are summarised in Table 3. Cr^{III} is coprecipitated quantitatively at pH 8 with $Fe(OH)_3$, and Cr^{VI} is either coprecipitated with cobalt pyrrolidinedithiocarbamate (CPDC) [154] or found from the difference between the total dissolved Cr, concentrated by coprecipitation on $Fe(OH)_2$ [111] or on $Bi(OH)_3$,[152,153] and Cr^{III}. Cr(inorganic) amounting to up to 60% of all dissolved forms of chromium has been detected for the first time in sea water[152,153]. This may be of considerable importance for other TE in NW, whose organic forms have not been studied.

Table 3. Methods for determining the chemical forms of TE by concentration on solid extracting agents*.

Chemical form of TE	Solid extracting agent	Method of determination	Refs.
Cr (III), Cr (VI)	$Fe(OH)_3$ and $Fe(OH)_2$	AAS	[111]
ditto	$Fe(OH)_3$ and $Bi(OH)_3$	ditto	[152, 153]
»	$Fe(OH)_3$ and CPDC	F	[154]
»	electrodeposition	AAS	[155]
Se (IV), Se (VI)	carbon	F	[50]
Hg(0)	Ag(0)	AAS	[156]
Me_2Hg			
As (III), As (V) , MAA	ion exchange resin	ditto	[157]
As (III), As (V) , MAA	ion exchange resin	AAS	[158]
ditto	ditto	DPP	[159]
Se (IV)	»	F	[160]
Se (VI)			
Cr (VI)	»	CL	[161]
V (IV), V (V)	»	NAA	[162]
Cr (III), Cr (VI)	»	ditto	[163]
ditto	»	AAS	[164]

*CDTC = cobalt pyrrolidinedithiocarbamate, F = fluorescent, CL = chemiluminescent.

Promising methods for concentrating other TE are the adsorption of Se^0 on active carbon after selective reduction of Se^{IV} by l-ascorbic acid[50] and the electrodeposition of Cr^{III}.[155] These methods detect down to 0.05 μg litre^{-1}. Volatile mercury compounds are blown from the sample, Hg^0 is amalgamated on a column of silver wool, and Me_2Hg after thermal decomposition at 900 °C. The detection limit is 0.001 μg litre^{-1}.[156]

Cation- and anion-exchange resins are used both to concentrate and to separate the chemical forms of TE. In the case of Se^{IV}, dithiocarbamate is added to the specimen before concentration on the resin[160]. The detection limit is 2 μg litre^{-1} [158] or 10 μg litre^{-1} [157] for the forms of As^V, 0.005 μg litre^{-1} for Cr^{VI},[161] and 0.01 μg litre^{-1} for the forms of V.[162]

Because of the appreciable stability in water and relative simplicity of the preparation of the hydrides of a number of TE, considerable use has recently been made of methods for determining the chemical forms of TE, in which, depending on the pH of the sample, the forms of TE are selectively reduced by $NaBH_4$ to the corresponding hydrides, which are then concentrated by blowing out in a stream of helium into cryogenic traps cooled with liquid nitrogen. The

hydrides, after separation by GLC or successive evaporation, are determined by various analytical methods (Table 4). The detection limit may reach thousandths of a microgram per litre[49,165,166,169,171] or less[44,168,170]. The interfering action of various cations and anions in the reduction by $NaBH_4$ has been studied, and it has been shown that the actual concentrations in most NW do not interfere in the determination of the forms of the TE.[165,168–170]. The use of EDTA as a masking agent has been proposed[167]. The distribution in NW has been determined for the forms of As,[44,165–167] Sb,[168] Se,[49] Ge,[169] and Sn.[170,171]

Table 4. Methods for determining the chemical forms of TE with hydride formation.

Chemical form of TE	Method of concentration	Method of determination	Refs.
As (III) + As (V), MAA DMAA	cryogenic trap	ES	[165]
As (III), As (V), MAA, DMAA	ditto	AAS	[166]
ditto	»	AAS-GLC	[44]
»	»	AAS	[167]
Sb (III), Sb (V), MSA*, DMSA	»	ditto	[168]
Ge (IV), MeGe (IV), Me_2Ge (IV)	cryogenic trap	ES	[169]
Se (IV)	ditto	AAS	[49]
Se (VI)			
Me_nSn(IV) (n=0–3)	»	ES	[170]
R_nSn (IV) (R = Me, n-Bu, n=1–3; R=Ph, n=1; R=Et, n=2, 3)	»	AAS	[171]
Sn (IV)			
Se (IV)	$Fe(OH)_3$	ditto	[172]
Ph_nSn (IV) (n=1–4)	hexane	GLC	[173]

*MSA = methylstibonic acid, DMSA = dimethylstibinic acid.

Se^{IV}, Se^{VI}, Te^{IV}, and Te^{VI} are determined by AAS without the separation and concentration of the hydrides[174], but serious difficulties may be encountered in the interpretation of the results when this method is used for the determination of As^{III}, As^{V},[174,175] Sb^{III}, and Sb^{V},[174] in particular because of the influence of the oxidation state of the TE hydride on the magnitude of its AAS signal[174].

The reduction of the forms of TE can be carried out, however, not in the sample but after their concentration by precipitation with $Fe(OH)_3$ [172] or by extraction with hexane[173]. The detection limits are <1 μg litre^{-1} and <10 μg litre^{-1} respectively.

* * *

The methods for determining the physicochemical forms of TE in NW are only beginning to be developed. The main difficulties are the insufficient sensitivity of the analytical methods and the consequent need to concentrate the forms for the determination; this generally leads to breakdown of their natural equilibrium and to uncertainty in the relationship between the measured and actual forms present in water. The question of the bio-availability of the forms of TE and related analytical problems are poorly understood and have been little studied. Greatest attention should therefore be paid to these problems in the future.

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Nitronium Salts in Organic Chemistry

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The review is devoted to the methods of synthesis and properties of nitronium salts. The characteristics of the nitration of various classes of organic compounds by nitronium salts are considered and new aspects of the mechanism of the nitration of aromatic compounds, discovered following the application of nitronium salts, are discussed.
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I. INTRODUCTION

The first solid nitronium salts were synthesised by Hantzsch in 1925. In the 1950's general methods were developed for the synthesis of nitronium salts and these compounds became available as reagents. The introduction of new nitrating agents into chemical practice was very important for the study of nitronium salts. Firstly, nitronium salts have many specific properties and their application greatly expands the synthetic possibilities of the nitration reaction. Secondly, the study of the characteristics of the nitration of aromatic compounds by nitronium salts and the discussion which arose in connection with this problem in the last 10–15 years have played a major role in the further development of our ideas about the nitration mechanism.

There have been few surveys of the literature on nitronium salts—after the review of Olah and Kuhn[1] in 1964, in which data relating to the initial investigation of this class of compound were compiled, no new reviews were published. The literature published up to 1980 is used in the present review.

II. SYNTHESIS AND PROPERTIES OF NITRONIUM SALTS

1. Synthesis of Nitronium Salts

Nitronium salts are ionic compounds containing the NO_2^+ cation and the anions of Lewis oxy-acids or complex acids—ClO_4^-, HSO_4^-, FSO_3^-, SO_4^{2-}, BF_4^-, PF_6^-, etc. The structure of nitronium salts was not established correctly immediately. Hantzsch[2] attributed the structures of nitracidium perchlorate $[H_2NO_3]^+ClO_4^-$ and dinitracidium perchlorate $[H_3NO_3]^{2+}2ClO_4^-$ to the nitronium perchlorate which he obtained for the first time. Later other workers[3,4] reproduced Hantzsch's synthesis and showed that his compounds are simply mixtures of nitronium perchlorate ($NO_2^+ClO_4^-$) and hydronium perchlorate ($H_3O^+ClO_4^-$).

Nitronium perchlorate can be obtained in several ways: by the reaction of nitrogen pentoxide with perchloric acid[3] or of nitrogen oxides with ozone and dry chlorine oxide[5], by the reaction of ClO_2F with nitric acid[6], or by the reaction between nitric acid and chlorine heptoxide[7]. Nowadays the most widely used method involves the synthesis of $NO_2^+ClO_4^-$ from ozone, nitrogen oxides, and chlorine oxide[8–10]. Another chlorine-containing nitronium salt, namely nitronium hexachloroantimonate, has been obtained by the reaction of antimony pentachloride with nitryl chloride in liquid chlorine[11]:

$$NO_2Cl + SbCl_5 \xrightarrow{Cl_2} NO_2^+SbCl_6^-$$

The synthesis and study of the properties of stable nitronium salts based on fluorine-containing Lewis acids have received considerable attention. Several general and specific methods of synthesis of these compounds have been proposed. Woolf and Emeleus[12–14] obtained $NO_2^+BF_4^-$, $NO_2^+PF_6^-$, $NO_2^+AsF_6^-$, $NO_2^+SbF_6^-$, $(NO_2)_2^{2+}SnF_6^{2-}$, $NO_2^+AuF_4^-$, and $NO_2^+FSO_3^-$ by the reaction of nitrogen dioxide with bromine trifluoride and the corresponding oxide (for example, boron oxide) or halide. $NO_2^+VF_6^-$, $NO_2^+NbF_6^-$, and $NO_2^+TaF_6^-$ were synthesised by the same method[15]:

$$NO_2 + B_2O_3 + BrF_3 \rightarrow NO_2^+BF_4^- ,$$
$$NO_2 + PBr_5 + BrF_3 \rightarrow NO_2^+PF_6^- .$$

Aynsley et al.[16] developed a general method of synthesis of nitronium salts by the reaction of nitryl fluoride with metalloids or their fluorides[17,18]:

$$Si + 6NO_2F \rightarrow (NO_2)_2^+SiF_6^- + 4NO_2 ,$$
$$BF_3 + NO_2F \rightarrow NO_2^+BF_4^- .$$

The reactions of oxides (V_2O_5, SO_3, etc.) with an excess of nitryl fluoride also lead to the formation of nitronium salts, for example:

$$SO_3 + NO_2F \rightarrow NO_2^+SO_3F^- .$$

The corresponding nitronium salts has been synthesised by the reaction of nitrogen dioxide with iridium hexafluoride[19].

The above methods of synthesis of nitronium salts are complex and require the use of compounds such as BrF_3 and NO_2F, which are difficult to obtain.

Nitronium salts became readily available reagents for extensive laboratory use only after the studies of Schmeisser and Elisher[20] and also Olah and co-workers[21], who showed that stable fluorine-containing nitronium salts can be obtained by the reaction of nitrogen pentoxide, anhydrous hydrogen fluoride, and a fluorine-containing Lewis acid in nitromethane:

$$N_2O_5 + HF + BF_3 \rightarrow NO_2^+BF_4^- + HNO_3 .$$

The replacement of N_2O_5 by concentrated nitric acids made it possible to simplify still further the synthesis of nitronium tetrafluoroborate[22,23]:

$$HNO_3 + HF + 2BF_3 \rightarrow NO_2^+BF_4^- + BF_3 \cdot H_2O .$$

Other Lewis acids, for example, phosphorus pentafluoride, arsenic pentafluoride, etc., react in the same way[22,24].

When it is necessary to obtain a salt free of an admixture of a nitrosonium salt, it is possible to employ modified methods in which the nitronium cation is generated from alkyl nitrates[25]

or nitryl chloride[26]:

$$RONO_2 + HF + 2BF_3 \rightarrow NO_2^+BF_4^- + ROH \cdot BF_3,$$

$$NO_2Cl + HF + 2BF_3 \rightarrow NO_2^+BF_4^- + HCl \cdot BF_3,$$

The nitronium salt of one of the strongest acids, namely trifluoromethanesulphonic, has been obtained recently[27-29].

Fairly convenient methods of synthesis of various nitronium salts have now been developed. Nitronium tetrafluoroborate, nitronium hexafluorosilicate, nitronium hexafluorophosphate, nitronium hexafluoroantimonate, and nitronium trifluoromethanesulphonate have found most applications as nitrating agents.

2. Physicochemical Properties of Solutions of Nitronium Salts

The solubility of nitronium salts has been inadequately studied. Nitronium tetrafluoroborate (NTFB) and nitronium fluorosulphonate[30] have been most fully investigated (see Table).

The solubilities of nitronium salts at 20 °C.

Solvent	Solubility, wt.%	
	NTFB	nitronium fluorosulphonate
Acetonitrile	3.1	1.6
Nitromethane	1.2	1.0
1,4-Dioxan	1.2	0.3
Methyl ether of ethylene glycol acetate	0.7	—
Methyl acetate	4.1	3.8
Ethyl acetate	0.1	0.1
Trimethyl phosphate	19.9	12.7
Tripropyl phosphate	6.0	5.4
Tributyl phosphate	1.9	1.6

NTFB dissolves only slightly in nitroethane and nitropropanes[1,31]. The rate of dissolution of NTFB is determined by diffusion processes and varies in parallel with its solubility in a number of solvents[30].

Nitronium hexafluoroantimonate, hexafluorophosphate, and hexafluoroarsenate are more soluble in organic solvents than NTFB and 50% solutions of these salts can be obtained for example in nitromethane.

The salts also dissolve readily in nitroethane, nitropropanes, sulpholane, and trifluoroacetic acid[31]. Less than 0.3% of NTFB and ~0.5% of $NO_2^+ClO_4^-$ dissolve in nitromethane at 25 °C.[21,31] The saturated NTFB solution in sulpholane at 25 °C contains 7% of the salt, while that in acetonitrile contains 10% of the salt. The solubility of NTFB in nitroethane and nitropropane is insignificant but there are no quantitative data[1,31].

A solution of NTFB in liquid hydrofluoric acid is a true electrolyte, like a KBF_4 solution[32]. Cryoscopic studies of NTFB solutions in sulpholane[31] showed that, at a concentration of ~ 3 mole %, NTFB exists in the form of ion pairs, of which less than 2% are dissociated into ions. With increase of the NTFB concentration in sulpholane, the conductivity of the salt rises linearly[21,27,31]. Solutions of nitronium trifluoromethanesulphonate[27] and NTFB[21] have very similar specific conductances. Conductimetric measurements on solutions of nitronium salts of monobasic and dibasic acids have shown that the nature of the anion has little influence on the degree of dissociation of the salt[33]. A solution of nitronium perchlorate in nitromethane is less than 6% dissociated[1].

On the basis of cryoscopic[34] and other data, Olah and Kuhn[1] believe that in concentrated solutions nitronium salts exist in the form of conducting ion triplets. On dilution of the solution, the triplets are converted into non-conducting ion pairs. Further dilution of the solution leads to the separation of the ion pairs into simple ions, which are also conducting; this enabled the authors to account for the minimum in the conductivity of nitronium perchlorate solutions in nitromethane with increase of the nitronium salt concentration. A conductivity minimum has also been observed for solutions of a series of uni-uni- and uni-bi-valent solutions of nitronium salts in ethyl acetate[33] and is also due to the existence of ionic associated species. On the other hand, a linear relation has been found[35] between the specific conductance of a solution of nitronium hexafluorophosphate in nitromethane and the concentration, no signs of the formation of ionic associated species being observed up to a nitronium salt concentration of 0.4 M.

The interpretation of the conductimetric data for nitronium salts in aprotic solvents is at present obscure. The problem is complicated by the fact that many physicochemical characteristics of nitronium salts in organic solvents and particularly their stability and electrical conductivity are to a large extent determined by the content of moisture and impurities and also by the nature of the interaction with the solvent employed. However, in the communications published up to 1970[1,21,31,36] no characteristics of the impurity and water contents in the solvents are given, which is the reason for the contradictory nature of the results.

Spectroscopic studies have been particularly important for the elucidation of the structure of nitronium salts. The study of infrared spectra led to the conclusion that nitronium ions have a linear structure in solution[37]. In nitronium perchlorate crystals the linearity of the nitronium ion breaks down[36,38]. Studies of the infrared and Raman spectra of a series of nitronium salts have led to the conclusion[39] that the nitronium ion in NO_2-X compounds is bent and that the amount of ionic character of the NO_2-X bond increases in parallel with the ONO angle in the sequence $NO_2Cl < NO_2F < NO_2^+SO_3F^- < NO_2^+S_2O_6F^- < NO_2^+ClO_4^- = NO_2^+BF_4^-$. These results are extremely interesting but they require additional tests, particularly since some experimental data do not agree with the measurements of other workers[27].

III. NITRATION BY NITRONIUM SALTS

An extremely important stage in the research into nitronium salts involves the choice of solvent. As mentioned above, nitronium salts have a limited solubility and interact with the majority of organic solvents. Solvents such as acetonitrile, acetic and phosphoric acid esters, nitromethane, dioxane, and sulpholane are usually employed for nitration. Nitroderivatives of aromatic hydrocarbons have been synthesised in an excess of the aromatic compound or in ether[21]. However, ethyl ether interacts with NTFB on mixing. Apart from the solvents indicated, aliphatic hydrocarbons, methylene chloride, and acetic anhydride have been used for nitration by nitronium salts. Nitration by NTFB has been carried out[40] in anhydrous acetic acid, but the latter interacts with NTFB at room temperature to form another nitrating agent—acetyl nitrate.

Nitration by nitronium salts is complicated by the liberation of the corresponding inorganic acids (tetrafluoroboric, hexafluorosilicic, etc.) which can also react in their turn

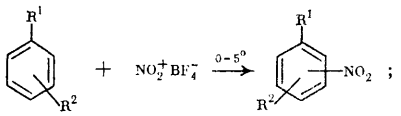
with the solvent, particularly since many of these acids are superacids (for example, trifluoromethanesulphonic acid is 14 times stronger than sulphuric acid[28]).

Some investigators have used solutions of nitronium salts in strong protic acids for nitration—sulphuric[28,40,41], methanesulphonic[40], trifluoromethanesulphonic[28], and fluorosulphonic[41]. However, such nitrating systems differ from the corresponding nitric acid solutions only by the water content and the acidity of the medium and will not be considered in this review.

1. Nitration of Aromatic Hydrocarbons

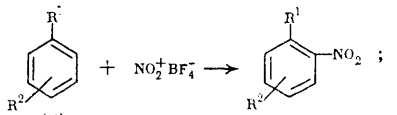
In 1950 it was observed[3] that a solution of nitronium perchlorate in nitromethane nitrates benzene to nitrobenzene almost instantaneously and slowly converts nitrobenzene into dinitrobenzene. However, the low stability of nitronium perchlorate and the risk of the explosion of its mixtures with organic solvents inhibited further investigation of the nitrating activity of this salt.

Olah and Kuhn were the first to carry out extensive studies on nitronium salts as nitrating agents. They showed that not only nitronium perchlorate but also other stable nitronium salts, namely the tetrafluoroborate, hexafluorosilicate, and hexafluoroantimonate, are active nitrating agents[1,21,42]. They investigated NTFB most fully and showed that, in sulpholane[22] or an excess of the substrate[42], $NO_2^+BF_4^-$ nitrates benzene and alkylbenzenes (I) very readily to the corresponding mononitro-derivatives in 80–95% yield:



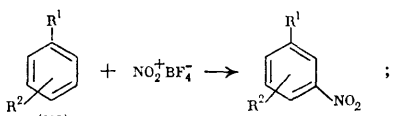
(a) $R^1=H$; $R^2=H$, CH_3, C_2H_5, iso-C_3H_7, n-C_3H_7, n-C_4H_9, iso-C_4H_9, or t-C_4H_9;
(b) $R^1=CH_3$; $R^2=CH_3$(o-, *m*-, or *p*-).

Monohalogenobenzenes react under approximately the same conditions, while dihalogenobenzenes are nitrated at a higher temperature (30–50 °C), but the yield is in all cases 80–90%. The nitration of benzene derivatives containing other electron-accepting substituents takes place just as successfully although the reaction is in this case slower and takes place at a higher temperature (up to 40–50 °C, in a few instances 90–100 °C). By nitrating *o*-tolunitrile with NTFB in sulpholane, it proved possible to obtain for the first time 3-dinitro-*o*-tolunitrile in 75% yield[1]. The reactions with other nitrating agents lead to the oxidation of the nitrile group:



(II)

(a) $R^1=Cl$, $R^2=o\text{-}NO_2$, $p\text{-}NO_2$; (b) $R^1=F$, $R^2=o\text{-}NO_2$, $p\text{-}NO_2$;



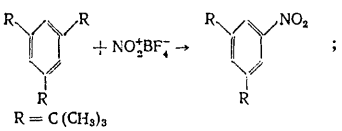
(III)

(a) $R^1=NO_2$, CN, $COOCH_3$, COCl, COF; $R^2=H$; (b) $R^1=CN$, $R^2=o\text{-}NO_2$; $m\text{-}NO_2$; $p\text{-}NO_2$; (c) $R^1=COOC_2H_5$, $R^2=m\text{-}NO_2$.

The readily oxidisable triaryl- and alkyldiaryl-phosphines were nitrated for the first time with NTFB and a series of *meta*-nitro-derivatives of arylphosphines were obtained[43].

The nitration of alkylbenzenes containing the isopropyl or t-butyl group with $NO_2^+BF_4^-$ is accompanied by substitutional nitration with elimination of one of the alkyl groups (*ipso*-substitution)[44]. In the nitration of *p*- and *o*-cumenes the degrees of substitution of the isopropyl group are 9.5 and 41% respectively. In the nitration of 1,4-di-isopropylbenzene one of the isopropyl groups is 56% substituted, while in the nitration of 1,4-di-t-butylbenzene the degree of substitution of the t-butyl group is 20%.

Steric hindrance interferes with the direct nitration of 1,3,5-tri-t-butyl-benzene: on treatment with NTFB, only substitutional nitration takes place with formation of 1,3-di-t-butyl-5-nitrobenzene:

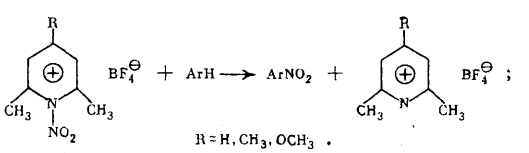


$R = C(CH_3)_3$

The interaction of polyalkylbenzenes with nitronium salts also leads to different hydroxymethyl derivatives[45,46]. Polynuclear aromatic compounds (biphenyl, naphthalene, and phenanthrene) are nitrated quantitatively by NO_2BF_4,[1] more than 50% of α-nitronaphthalene being obtained from naphthalene and only 9-nitrophenanthrene being formed from phenanthrene.

Comparison of the nitrating capacities of three nitronium salts, namely the tetrafluoroborate, the hexafluorophosphate, and the trifluoromethanesulphonate, with respect to toluene showed that the highest reaction rate or the highest yield of nitrotoluene are obtained when nitronium trifluoromethanesulphonate is used[28]. On the other hand, Olah and Kuhn[47] were unable to detect the influence of the nature of the anion on the yield of *o*-nitrotoluene; they explained the decrease of the content of the *ortho*-isomer from 65 to 55% on passing from sulpholane to nitromethane and toluene by the difference between the degrees of solvation of the ion pairs of the nitrating agent. In the nitration of toluene by nitronium trifluoromethanesulphonate in alkyl halides, the ratio of the *ortho*- and *para*-isomers at temperatures between −60° and −90 °C remains almost constant at 1.63, while at −110 °C it decreases to 1.03. The yield of the *meta*-isomer does not exceed 0.33% under these conditions[47].

Alkylnitropyridinium salts are interesting nitrating agents. The alkyl groups in the 2- and 6-positions of pyridine (VI) prevent the conjugation of the nitro-group with the ring (owing to their non-coplanarity), which leads to a high nitrating capacity of these salts. In contrast to inorganic nitronium salts, pyridinium salts make it possible to carry out nitration readily under homogeneous conditions. Furthermore, the acid formed as a result of the reaction is bound by alkylpyridine, which is very important in the nitration of compounds sensitive to the action of acids[48]:



(IV)

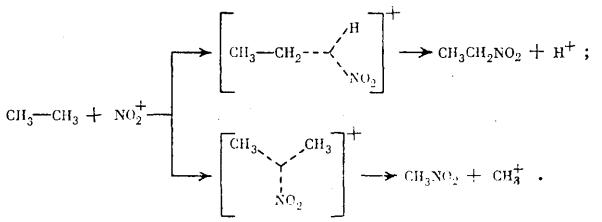
R = H, CH_3, OCH_3 .

The solvent apparently has a considerable influence on the nitrating activity of nitronium salts, but this problem has as yet been little investigated.

2. Nitration at a Saturated Carbon Atom

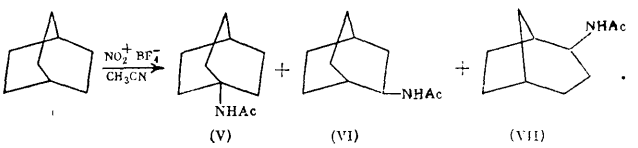
All the nitration reactions of paraffinic and naphthenic hydrocarbons known hitherto take place via a free-radical mechanism involving the $NO_2^{\cdot}$ radical[108]. It has been shown only recently[49] that the nitration of paraffinic hydrocarbons can be achieved with the aid of stable nitronium salts in the methylene chloride–sulpholane system under conditions which virtually rule out the formation of the radicals. Thus the authors obtained nitromethane from methane, albeit with a low yield, nitroethane from ethane, etc. The tertiary C–H bond exhibits the highest reactivity: adamantane is nitrated to 1-nitroadamantane in 10% yield. Nitronium salts can be replaced by the nitro-group and a proton in a methyl group of polyalkylbenzenes[46].

The nitration of paraffinic hydrocarbons is accompanied by nitrolysis with the dissociation of a C–C bond, the process occurring more readily than the nitration at secondary and primary carbon atoms. The nitration of alkanes with the normal structure therefore results in the preferential formation of nitrolysis products. For example, a mixture of 1- and 2-nitrobutanes, nitroethane, and nitromethane has been obtained from n-butane in proportions of 1:1.5:4:5, while a mixture of t-nitrobutane and nitromethane in proportions of 3:1 was obtained from isobutane. According to Olah's hypothesis[50], nitration, like other electrophilic processes (deuterium exchange, alkylation, and acid-catalysed isomerisation), proceeds via the "frontal" attack on a C–H or C–C bond with formation of a triangular transition state and not via the attack by the electrophile on a tetragonal carbon atom:



In the first excited state the linear nitronium cation can be converted into the bent form[51] and can react as an electrophile.

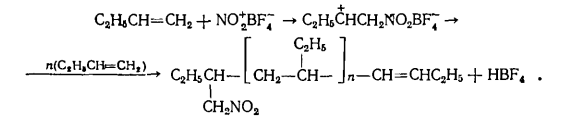
The nitronium cation is also capable of oxidising secondary and particularly tertiary carbon atoms with formation of a carbenium ion[52]. If the reaction takes place in acetonitrile, then the carbocation is converted by the Ritter reaction into the corresponding amide. Thus *N*-(1-adamantyl)acetamide was obtained from adamantane (yield 88%) and *N*-(*exo*-2-norbornyl)acetamide was obtained from norbornane (yield 78%). Bicyclo[2.2.2]octane is converted in 73% yield into the corresponding amides (V)–(VII) in proportions of 65:22:13:



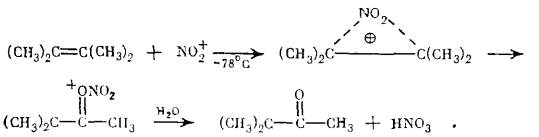
It is striking that the ratio of isomers (VI) and (VII) formed is approximately the same as in the similar isomerisation of the carbocation obtained in the solvolysis of bicyclo[2.2.2]-octyl-2-*p*-bromobenzenesulphonate[53,54], which is also evidence in support of an ionic mechanism of the reaction of polycyclanes with NTFB under consideration. Both *exo*- and *endo*-2-norbornyl bromides react analogously with nitronium salts[55].

3. Nitration at the Double Bond

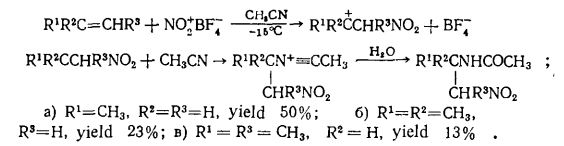
The reactions of nitronium salts with olefins do not take place unambiguously and depend to a large extent on the nature of the alkene and the reaction conditions. When alkenes react with nitronium salts, a reactive nitrocarbenium ion, which can initiate polymerisation, is formed[56]:



The nitrocarbenium ion can be also stabilised as a result of an intramolecular rearrangement to the oxonium ions. The latter reacts with water to form a ketone[57]:

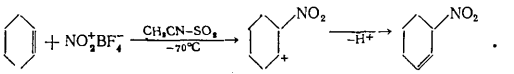


If the nitration of olefins by nitronium salts is carried out in acetonitrile, then the nitrocarbenium ion undergoes the Ritter reaction with the solvent to form nitroacetamides[58]:

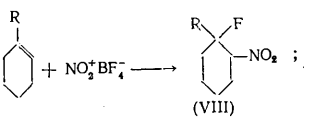


a) $R^1=CH_3$, $R^2=R^3=H$, yield 50%; б) $R^1=R^2=CH_3$, $R^3=H$, yield 23%; в) $R^1=R^3=CH_3$, $R^2=H$, yield 13%.

The mode of the reaction between olefins and nitronium salts depends on the structure of the substrate and the process conditions. For example, cyclohexene reacts with NTFB to form a nitrocarbocation, which is stabilised in the form of 3-nitrocyclohexene (yield 40%)[59,60]:



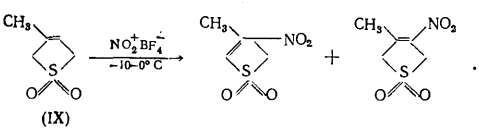
The nitration of 1-substituted cyclohexenes is accompanied by the formation of 2-fluoro-1-nitro-2-R-cyclohexanes (VIII):



(a) R = CH_3, yield 30% [61]; (b) R = Cl, yield 60%.[62]

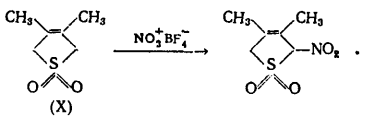
The mechanism of the formation of the fluoro-derivative has not been studied but the stereochemistry of the process has attracted attention—the reaction proceeds via a vicinal-addition mechanism[61].

Alkenes with a reduced electron density, for example 3-methyl-2,5-dihydrothiophen 1,1-dioxide (IX), react with NTFB more or less unambiguously:



The reaction of 3,4-dimethyl-2,5-dihydrothiophen 1,1-dioxide (X), in which the double bond is blocked by the methyl groups, apparently proceeds via an electrophilic substitution

mechanism[63]:



(X)

As mentioned above, the reactions of nitronium salts with olefins proceed via the formation of a nitrocarbocation and the decisive factor which determines the success of the reaction is the ease of the stabilisation of nitrocarbocation by its conversion into the final product. One of the methods for such stabilisation involves nitration in acetic anhydride. It has been suggested that the complex $NO_2^+BF_4^-.Ac_2O$ reacts and that 2-acetoxy-1-nitroalkane is obtained in 36–60% yield after the hydrolysis of the reaction mixture with water[64]. The reaction involves mainly *cis*-addition:

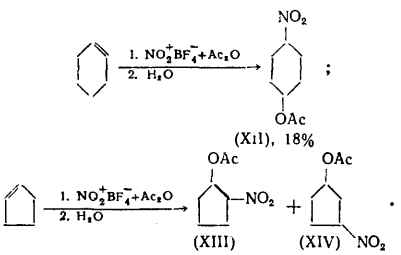
$$R^1R^2C{=}CHR^3 + NO_2^+BF_4^- \xrightarrow{Ac_2O,\,H_2O} AcOCR^1R^2CHR^3NO_2 \ ;$$

(XI)

a) $R^1{=}CH_3$, $R^2{=}R^3{=}H$; б) $R^1{=}R^2{=}CH_3$ (*cis, trans*), $R^3{=}H$; в) $R^1{=}R^2{=}CH_3$, $R^3{=}H$

4-Acetoxy-4-methyl-2-pentanone was isolated together with the nitroacetate (XIc) after the nitration of isobutene, which indicates the formation of an acylium cation in the reaction mixture.

The nitration of cyclenes is as a rule accompanied by the transfer of the reaction centre and the formation of the β- and γ-nitroacetates (XII)–(XIV) in 18–29% yields[65]:

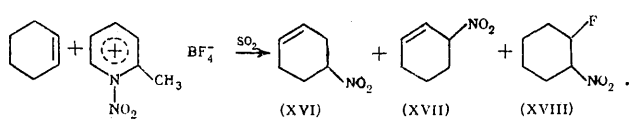


(XII), 18%

(XIII) (XIV)

The high degree of stabilisation of the nitrocarbocation in the nitration of norbornene in acetic anhydride ensures a high (86%) yield of two conformers of 2-acetoxy-7-nitrobicyclo[2.2.1]heptane formed.

Overall, one should say that the nitration of olefins, particularly those containing electron-donating substituents, by nitronium salts is complicated by side reactions and does not always lead to the expected result. In many instances nitration with nitronium tetrafluoroborate takes place with higher yields in the presence of α-picoline[62,66]. In this case the nitrating agent is apparently not the nitronium salt but 1-methyl-*N*-nitropyridinium tetrafluoroborate(XV), which is formed rapidly when NTFB is mixed with α-picoline[48]. The yields of products (XVI)–(XVIII) are respectively 40, 25, and 13%:



(XVI) (XVII) (XVIII)

The interaction of nitronium salts with the heteropolar C=N double bond in nitroalkane salts is of great interest. Olsen et al. showed that *gem*-dinitro-compounds are formed in the nitration of 2-nitropropane and nitrocyclohexane salts with NTFB in acetonitrile[67]:

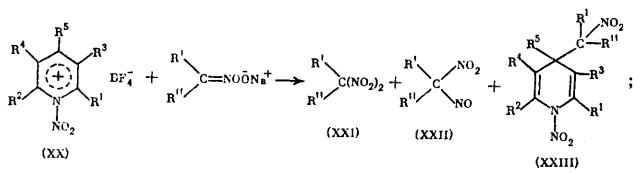
$$R^1R^2C{=}NO_2M + NO_2^+BF_4^- \rightarrow R^1R^2C(NO_2)_2 + MBF_4 \ ;$$

(XIX)

(a) M=Li, (b) M=Na, (c) M=K .

The reaction takes place between −35° and −40 °C and its character depends on the nature of the cation. When the lithium salt (XIXa) is used, the yield is 35%, in the presence of the sodium salt (XIXb) it is 25%, while the potassium salt (XIXc) does not react. Apart from the *gem*-dinitro-compounds, the nitration of nitroalkane salts gives rise also to the pseudonitroles $R^1R^2C(NO)NO_2$. In contrast to dinitroalkanes, their yield increases on passing from the lithium to the potassium salts from 5 to 25%.

N-Nitropyridinium tetrafluoroborate salts, which are very mild nitrating agents, can also be used for the nitration of mononitroparaffin salts[68,69]. However, the nitration is in this case complicated by the alkylation of the *N*-nitropyridinium salt of the nitroalkane and the formation of a pseudonitrole (for secondary nitro-compounds):



(XX) (XXI) (XXII) (XXIII)

(a) $R^1{=}R^2{=}R^3{=}R^4{=}R^5{=}H$; (b) $R^1{=}R^2{=}CH_3$, $R^3{=}R^4{=}R^5{=}H$; (c) $R^1{=}R^3{=}R^4{=}R^5{=}H$, $R^3{=}C_2H_5$; (d) $R^1{=}R^2{=}R^3{=}H$, $R^4{=}R^5{=}CH_3$; (e) $R'{=}CH_3$, $R''{=}H$; (f) $R'{=}C_2H_5$; $R''{=}H$; (g) $R'{=}R''{=}CH_3$; (h) $R'R''C$— cyclohexylidene

The extent of these side reactions depends on the structure of the nitrating agent. *N*-Nitropyridinium tetrafluoroborate (XXa) does not enter into the nitration reaction; only the alkylation product is formed—*N*-nitro-4-nitroalkyl-1,4-dihydropyridine [compounds (XXIII, a and e)–(XXIII, a and g)] in 60–85% yield. The introduction of substituents into the 4- and 2,6-positions of the pyridine ring [compounds (XX, b–c)] promotes the formation of the pseudonitroles (XXII, g and h) (up to 20%) and *gem*-dinitroalkanes (XXI, e–h), whose yield reaches 42%. Primary nitroalkanes react with 3,5-lutidine derivatives (XXd) to form mainly the alkylation products (XXIII, d and e), while secondary nitroalkanes give rise to the *gem*-dinitro-compounds (XXI, g and h) in yields up to 56%. The anion of 1,1-dinitroethane reacts with the salt (XXc) to form only the alkylation product (XXIIIc, $R' = CH_3$, $R'' = NO_2$).

An interesting example of nitration is the reaction of NTFB with the sulphonium dinitro ylide to form a trimethylsulphonium salt[70]:

$$(CH_3)_2\overset{+}{S}{-}\bar{C}(NO_2)_2 + NO_2^+BF_4^- \xrightarrow{CH_3CN} [(CH_3)_2\overset{+}{S}{-}C(NO_2)_3]\,BF_4^- \ .$$

Compounds containing three nitro-groups and an onium cation at the same carbon atom were previously unknown. Such derivatives of trinitromethylselenonium are less stable—all attempts to synthesise such compounds have led to the formation of tetranitromethane. The reaction can be formally regarded as electrophilic substitution at a saturated carbon atom attached to nitro-groups[71]:

$$(C_6H_5)_2\overset{+}{S}e{-}\bar{C}(NO_2)_2 + NO_2^+BF_4^- \xrightarrow{CH_3CN} C(NO_2)_4 \ .$$

NTFB reacts with aliphatic, carbocyclic, or aromatic ketoximes in the presence of pyridine to form the corresponding ketones[72].

NTFB reacts just as smoothly with ketone dimethylhydrazones:

$$\begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!C{=}N{-}N(CH_3)_2 \xrightarrow{NO_2^+BF_4^-} \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!C{=}O \ .$$

The reactions take place with high yields and can serve as a preparative method for the regeneration of ketones from their oximes and hydrazones.

4. Nitration at a Nitrogen Atom

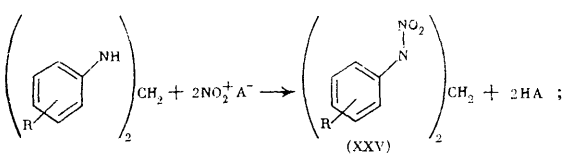
The first indication of the possibility of the nitration of amines by nitronium salts was given by Olah and Kuhn[1]. Olsen et al.[67] found that NTFB reacts readily with secondary amines in methylene chloride or acetonitrile to form *N*-nitroamines (XXIV), whose yield is 50–70%:

$$2R^2NH + NO_2^+BF_4^- \rightarrow R^2N{-}NO_2 + R^2NH_2 + BF_4^- \ ;$$
(XXIV)
$R^2 = (C_4H_9)_2$, $(NCCH_2CH_2^-)_2$, or morpholinyl .

In a later study[73] it was shown that the nitration of aromatic amines proceeds differently depending on their basicity. Amines of moderate and low basicity, namely bis(2-cyanoethyl)amine ($pK_a = 5.25$), bis(2,2-dinitropropyl)amine ($pK_a = 3.08$), and bis(2,2,2-trinitroethyl)amine ($pK_a = 0.05$) are nitrated by NTFB to the corresponding *N*-nitroamines in acetonitrile or ethyl acetate in yields of 87–98%. Despite the data of Olsen et al.[67], the nitration of highly basic dialkylamines ($pK_a = 8.70–11.25$) is accompanied by the partial reduction of $NO_2^+BF_4^-$ to nitrosonium tetrafluoroborate and the formation of nitrosoamines. The content of nitrosoamine in the reaction mixture increases with increase of the reaction temperature. Nitronium hexafluorosilicate proved to be a milder nitrating agent; its application makes it possible to reduce greatly the formation of nitroso-derivatives.

The nitration of aliphatic-aromatic amines also proceeds smoothly and the low acidity of the medium makes it possible virtually to avoid the *N*-nitro-*C*-nitro-rearrangements[73].

Aromatic methylenebisamines, which are unstable in an acid medium, were nitrated for the first time with nitronium salts and *N,N'*-diarylmethylenedinitroamines (XXV) were obtained in a high yield[74]:



$A^- = BF_4^-, SiF_6^{2-}$; R = 2-NO_2, 3-NO_2, 4-NO_2, 2,6- and 3,5-$(NO_2)_2$.

The reactions of nitronium salts and nitrogen pentoxide with ammonia have been investigated[24,39,75,76] and it has been shown that nitramide (XXVI) is formed at the temperature of liquid nitrogen:

$$2NH_3 + NO_2^+A^- \rightarrow NH_2NO_2 + NH_4^+A^- \ ;$$
(XXVI)
$A^- = SO_3F^-, ClO_4^-, BF_4^-, NO_3^-$.

The formation of nitramide is determined by the nature of the anion: on passing from nitronium chlorosulphonate to NTFB, the yield increases from 8 to 43%.

On treatment with nitronium salts, primary aliphatic amines are converted into alkyl nitrates (apparently via diazotisation by the nitronium cation), but *N*-2,4,6-tetranitroaniline was obtained in a high yield from the weakly basic picramide[67].

Nitronium salts proved to be particularly useful in the synthesis of *N,N*-dinitroamines which had been previously difficult to obtain. It was shown[77] that the interaction of primary nitroamines with NTFB, nitronium pyrosulphate, fluorosulphonate, fluorosilicate, as well as other nitronium salts leads to the formation of the *N,N*-dinitroamines (XXVII):

$$RN(NO_2)X + NO_2^+A^- \rightarrow RN(NO_2)_2 \ ;$$
(XXVII)
X=H, NH_4, K, Li etc. ; $A = BF_4^-, S_2O_7^{2-}, FSO_3^-, SiF_6^{2-}, ClO_4^-, SbF_6^-, SnF_6^{2-}$.

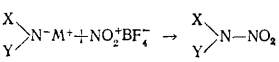
Aliphatic and aromatic amines, including those with other functional groups, readily participate in the reaction. According to the authors' data, best results are obtained in nitration by nitroamine salts in chloroalkanes or acetonitrile. However, the employment of more basic solvents, such as ethers and esters, ensures equally high yields in the nitration of both free nitroamines and their salts[78].

Olsen et al.[67] suggested that NTFB be used in acetonitrile or methylenechloride for the synthesis of the primary nitroamides (XXVIII):

$$RCONH_2 + NO_2^+BF_4^- \rightarrow RCONHNO_2 + HBF_4 \ ;$$
(XXVIII)
$$HBF_4 + KOCOCH_3 \rightarrow KBF_4 + CH_3COOH \ .$$

The nitroamides of benzoic and chloroacetic acids were obtained in satisfactory yields by the method proposed, but the yield of nitroacetamide was only 12%. This can be explained by the fact that the aliphatic nitroamides are hydrolysed in the solvents indicated even in the presence of potassium acetate. Only the use of more basic solvents—ethyl acetate, 1,4-dioxan, or trimethyl phosphate—made it possible to obtain nitroamides of different structure in 40–90% yield[79]. Succinimide is nitrated by NTFB in ethyl acetate in 43% yield[67].

The general method of synthesis of sulphonic acid nitroimides (XXIX) consists in the reaction of NTFB with imide salts[80]:

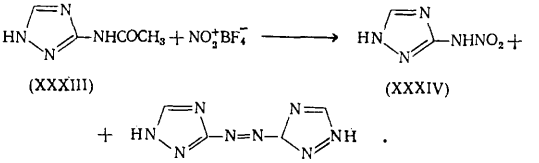


(XXIX)
(a) X=*n*-$CH_3C_6H_4SO_2$; Y=COOR; (b) X=Y=CH_3SO_2; $C_6H_5SO_2$

One of the known methods of synthesis of dialkylnitroamines involves the reaction of dialkylamides with nitric acid, which leads to the substitution of the acyl group by the nitro-group (nitrolysis). However, when nitric acid or its mixtures with acetic anhydrides are used, the yield of nitroamines is as a rule low and only the employment of the HNO_3–$(F_3CCO)_2O$ mixture makes it possible to raise it to 90%.[81] For preparative purposes, it is more convenient to nitrate the dialkylamides (XXX) by nitronium salts[82]. The reaction takes place at 20 °C in acetonitrile or esters. The dialkylnitroamines (XXXI) are formed in yields up to 90% and the acyl group is converted into acylium tetrafluoroborate (XXXII):

$$R_2NC(O)R' + NO_2^+BF_4^- \rightarrow R_2N{-}NO_2 + R'CO^+BF_4^- \ ;$$
(XXX) (XXXI) (XXXII)
R=CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, R'=CH_3, C_2H_5, CH_2CN, CH_2Cl, $CHCl_2$, CCl_3 .

The possibility of the nitrolysis of secondary amides with formation of the corresponding primary *N*-nitroamines (XXXIV) [together with 3,3'-azo-1,2,4-triazole (XXXV)] has been demonstrated for an *N*-acyl derivative of 3-amino-1,2,4-triazole (XXXIII)[83]:



(XXXIII) (XXXIV)
(XXXV)

Under the reaction conditions, alkyl-*N*-nitroamines decompose in the presence of the organic acids liberated[84]. Amides containing electron-accepting substituents at the nitrogen

atom also undergo nitrolysis by nitronium salts. Thus *N*-fluoronitroamines (XXXVI) were obtained from *N*-fluoroamides[85]:

$$RNFCOOCH_3 + NO_2^+BF_4^- \rightarrow \underset{\underset{F}{|}}{RNNO_2} \ ;$$

(XXXVI)

R=Alk .

Alkyl-*N*,*N*-dinitroamines (XXXVIII) are formed in high yields from *N*-alkyl-*N*-nitroamides (XXXVII)[84]:

$$\underset{\text{(XXXVII)}}{RN(NO)_2C(O)R'} + NO_2^+BF_4^- \rightarrow \underset{\text{(XXXVIII)}}{RN(NO_2)_2} + R'CO^+BF_4^- \ ;$$

R=CH_3, C_4H_9, R'=CH_3, C_3H_7, CCl_3 .

The reaction of NTFB with *N*-alkylamides has been investigated[67,84] under insufficiently comparable conditions, but nevertheless comparison of the results permits the conclusion that at a low temperature (−30 °C) *N*-butylacetamide and ethyl n-butylcarbamate in acetonitrile are nitrated to the *N*-nitro-derivatives[67], while at higher temperatures (up to +10 °C) nitrolysis takes place with formation of the corresponding carboxylic acid and an alcohol as well as N_2O.[86] The question of the order in which the C–N bond is *N*-nitrated and cleaved in the reactions of *N*-alkylamides with NTFB requires additional study. Aliphatic isocyanates react with NTFB in ethyl acetate or acetonitrile with formation (after hydrolysis) of alkylnitroamines[87]:

$$R(N{=}C{=}O)_n + NO_2^+BF_4^- \xrightarrow{+H_2O} RNHNO_2 + CO_2 + HBF_4 \ ;$$

n=1; R=C_2H_5, C_3H_7, C_4H_9; n=2; R=$(CH_2)_4$, $(CH_2)_6$.

The study of the nitration of a series of *N*,*N*-diacylmethylamines showed that the acetyl group is substituted by the nitro-group and, depending on the conditions and the component ratio, methylnitroacetamide or methyl-*N*,*N*-dinitroamine is formed[88]:

$$CH_3N(COCH_3)_2 + NO_2^+BF_4^- \begin{cases} \rightarrow CH_3N(NO)_2COCH_3 \ ; \\ \rightarrow CH_3N(NO_2)_2 \ . \end{cases}$$

The methanesulphonyl group can also be substituted by the nitro-group. The tosyl or an alkoxycarbonyl group do not enter into this kind of reaction.

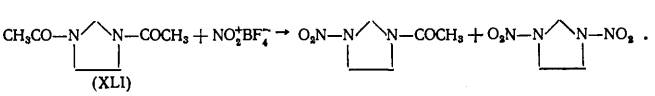
The mode of reaction of NTFB with substituted methylenediamines depends on the nature of the substituents[88,89]. Alkanesulphonyl, arenesulphonyl, or methoxycarbonyl derivatives (XXXIX) undergo nitrolysis at the C–N bond with formation of substituted nitroamines. This reaction pathway is favoured by the formation of the carbonium-immonium ion (XL) stabilised by the mesomeric effect of the amine nitrogen:

$$\underset{\underset{R''}{|}\ \underset{R''}{|}}{R'NCH_2NR'} + NO_2^+BF_4^- \rightarrow \underset{\underset{R''}{|}}{R'N{-}NO_2} + \underset{\underset{R''}{|}}{R'NCH_2^+}BF_4^- \ ;$$

(XXXIX) (XL)

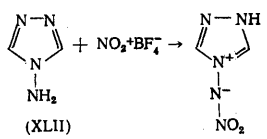
R'=Alk, R''=Alk, $SO_2C_6H_5$, $COOCH_3$.

N,*N*-Diacetylimidazolidine (XLI) undergoes substitutional nitration by nitronium salts to *N*-acetyl-*N'*-nitro- or *N*,*N'*-dinitro-derivatives:



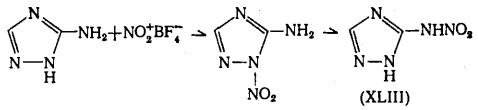
(XLI)

Nitronium salts are convenient nitrating agents for the synthesis of *N*-nitroimides. 4-Amino-1,2,4-triazole (XLII) reacts with NTFB in acetonitrile to form 4-nitroimino-1,2,4-triazole in 65% yield[90]:



(XLII)

1-Aminobenzimidazole is nitrated analogously, 1,1'-azobenzimidazole being formed as a side product. 3-Amino-1,2,4-triazole reacts with NTFB in acetonitrile to form *N*-nitrotriazole, which rearranges to the nitroaminotriazole (XLIII):



(XLIII)

Both nitronium and nitrosonium salts readily react with azodicarboxylate anions in accordance with the following scheme:

$$NO_2^+ + {}^-OOCN{=}NCOO^- \rightarrow N_2O_4 + 2CO_2 + N_2 \ .$$

The reaction of alkyl azodicarboxylates depends on the reactivity of the electrophilic species. NTFB, for example, reacts with ethyl azodicarboxylate, while the weaker electrophile nitrosonium tetrafluoroborate does not react.

The reaction of NTFB with lithium azide in acetonitrile results in the formation of covalent nitronium azide, which is converted into nitrous oxide above −10 °C[91]:

$$NO_2^+BF_4^- + LiN_3 \rightarrow LiBF_4 + NO_2N_3 \xrightarrow{\Delta} 2N_2O \ .$$

5. Nitration of Heterocyclic Compounds

The possibility of the nitration of heterocyclic compounds by nitronium salts was initially demonstrated in relation to pyridine[1,92,93]:

$$C_5H_5N + NO_2^+BF_4^- \rightarrow [C_5H_5NNO_2]^+BF_4^- \ .$$

In the presence of an excess of pyridine, the resulting salt is converted into derivatives of glutaconic aldehyde[92]:

$$[C_5H_5NNO_2]^+BF_4^- \xrightarrow{C_5H_5N} \left[C_5H_5^+NCH{=}CH{-}CH{=}\underset{\underset{NO_2}{|}}{CHCHN}\right]BF_4^- \rightarrow$$

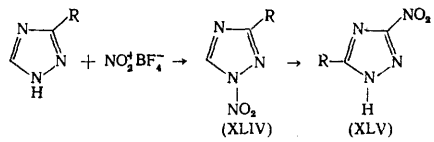
$$\xrightarrow{H_2O} [C_5H_5NCH{=}CHCH{=}CHCHO]^+BF_4^- \ .$$

N-Nitropyridinium salts are fairly stable and the N–C migration of the nitro-group is not observed even on heating. On the other hand, alkylnitropyridinium salts are "mild" nitrating agents (see Section III, subsection 1, subsection 3, and subsection 6).

Olah and Kuhn reported that thiophen[1] forms nitrothiophen in 91% yield on nitration with NO_2BF_4, while the nitration of furan results in a 14% yield of nitrofuran. 3-Nitro-6-phenyl-2-pyridone has been obtained in 40% yield by the nitration of 6-phenyl-2-pyridone with NTFB[94].

C-Nitroazoles are known to be difficult to synthesise by direct nitration with nitric acid. The use of NTFB in acetonitrile made it possible to obtain a series of 3-substituted 1,2,4-triazoles. The reaction proceeds via a stage involving

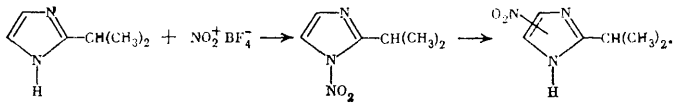
the formation of the *N*-nitro-derivative (XLIV), which isomerises to the *C*-nitro-compound (XLV)[95]:



(XLIV) (XLV)

R=H, CH_3, Cl, Br

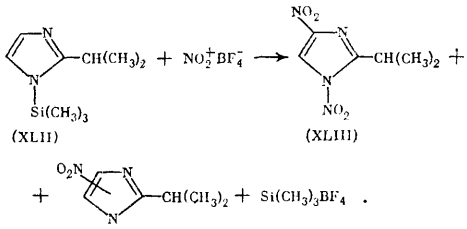
2-Isopropylimidazole (XLVI) is apparently nitrated analogously[96]:



(XLVI)

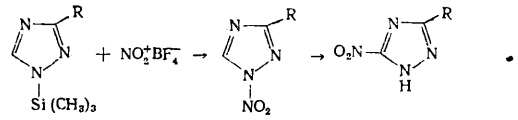
The yield of *C*-nitrotriazoles is as a rule low as a consequence of the dinitration of the *N*-nitro-compounds under the influence of fluoroboric acid formed on nitration.

A very interesting modification of this method, which rules out the formation of acid, has been proposed, namely one involving the nitration of trimethylsilyl derivatives. It has been shown for 2-isopropyl-1-trimethylsilylimidazole (XLVII) that this method makes it possible to obtain compounds which could not be synthesised previously, for example, 2-isopropyl-1,4-dinitroimidazole (XLVIII)[96]:



(XLVII) (XLIII)

The nitration of *N*-trimethylsilyl-1,2,4-triazoles (XLIX) makes it possible to obtain *N*-nitrotriazoles, which can be used to synthesise *C*-nitro-derivatives in yields up to 90%[95]:

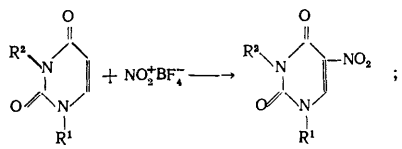


(XLIX)

R=H, CH_3, Cl, Br

Despite the additional labour involved in the synthesis of the trimethylsilyl derivatives, this method is most convenient for the preparation of 3(5)-nitro-1,2,4-triazoles.

Uracil and its 1-methyl and 1,3-dimethyl derivatives are nitrated to 5-nitro-derivatives (L) in high yields by NTFB in sulpholane:



(L)

R^1, R^2=H or CH_3 .

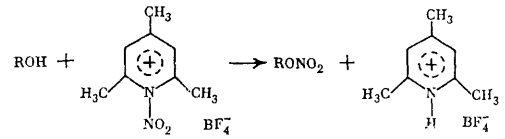
The attempts to nitrate a pyrimidine nucleoside (a 2'-deoxyglycoside) by NTFB as a rule leads to the degradation of the molecule or the formation of 5-nitrouracil, but the corresponding nucleotide (nucleoside 5'-monophosphate) is nitrated in the 5-position in the pyrimidine ring[97].

6. Nitration of Alcohols and Ethers

Aliphatic alcohols are readily nitrated by NTFB to the corresponding nitrates in 70–90% yields[98]:

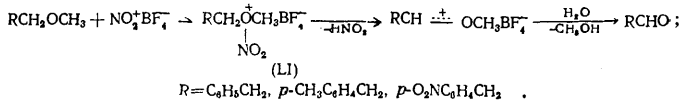
$$ROH + NO_2BF_4 \rightarrow RONO_2 + HBF_4 ;$$
R=Alk, $HalCH_2CH_2$, CF_3CH_2 .

The use of *N*-nitrocollidinium tetrafluoroborate in acetonitrile instead of a nitronium salt makes it possible to nitrate alcohols under milder, readily controlled conditions:



Aliphatic and carbocyclic alcohols enter into the reaction, the yield of nitrates being almost quantitative even in the nitration of the readily oxidisable diols and glycerol. It has been shown for benzyl alcohol that the reaction is fairly selective and permits nitration at the oxygen atom without involving the benzene ring[99].

Nitronium salts also react with the oxygen of the ether linkage. The nitroxonium ion (LI) formed in the reaction is readily converted, in high yields, into the corresponding aldehyde or ketone[100]:

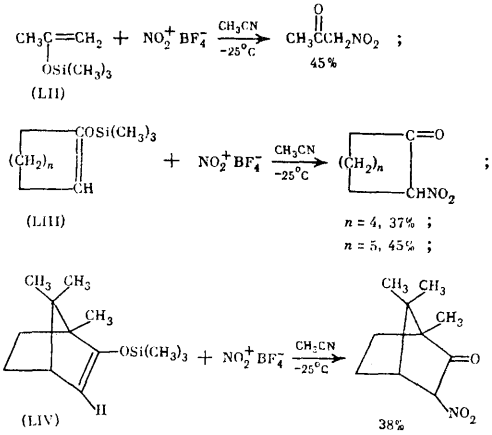


(LI)

R=$C_6H_5CH_2$, *p*-$CH_3C_6H_4CH_2$, *p*-$O_2NC_6H_4CH_2$.

The methyl ethers of cyclohexanol and cyclopentanol are converted into the methyl esters of the corresponding ω-hydroxyiminocarboxylic acids.

The nitration with nitronium salts of derivatives of the enolic vinyloxysilanes (LII)–(LLIV), leading to α-nitroketones which are usually difficult to obtain, is of special interest[101]:



(LII) 45%

(LIII) *n* = 4, 37% ; *n* = 5, 45% ;

(LIV) 38%

The reaction apparently proceeds via the formation of a substituted vinyl nitrate, which is comparatively stable in aprotic media and rearranges to an α-nitroketone.

7. Reactions of Nitronium Salts with Organoelemental and Complex Compounds

Diphenyl sulphide reacts with NTFB or $NO_2^+PF_6^-$ at −78 °C with formation of diphenyl sulphoxide. Dialkyl(aryl) selenides, triaryl(acyl)phosphines, triarylarsines, and triarylstibines undergo analogous reactions[102]. ^{13}C, ^{15}N, and ^{31}P NMR studies have shown that the reaction proceeds via the formation of the corresponding nitro-onium salts (LV), which are irreversibly converted into the nitrato-onium salts (LVI) and further into the corresponding oxides:

$$R{-}S{-}R' + NO_2^+ \rightleftarrows \underset{(LV)}{\left[\begin{array}{c} NO_2 \\ | \\ R{-}S{-}R' \end{array}\right]^+} \rightarrow \underset{(LVI)}{\left[\begin{array}{c} ONO \\ | \\ R{-}S{-}R' \end{array}\right]^+} \rightleftarrows \begin{array}{c} O \\ \uparrow \\ R{-}S{-}R' \end{array} + NO^+ .$$

This is the first reliably demonstrated instance of the isomerisation of a nitro-derivative to the *O*-nitrite. Similar reactions have also been postulated for $C{-}NO_2$ carbonium ions (see Section III, subsection 3).

Organotin compounds, for example, trimethylstannylacetylenes (LVII), undergo substitutional nitration by nitronium salts with formation of nitroacetylenes[103]:

$$\underset{(LVII)}{R_3SnC{\equiv}CR'} + NO_2^+BF_4^- \xrightarrow[-20^\circ]{} R'C{\equiv}CNO_2 + R_3SnBF_4 .$$

An analogous reaction of a derivative of another Group IV element (silicon) is described in subsection 5.

Ferrocenyl(triphenylphosphine)gold reacts with NTFB to form a complex mixture of products: ferrocene, biferrocenyl, [ferrocenyl(triphenylphosphine)gold]triphenylphosphinegold tetrafluoroborate[104]. The reaction of dichlorodicymantrenylstannane with NTFB is accompanied by the reduction of the latter[103] and proceeds via the mechanism

$$[C_5H_4Mn(CO_3)]_2SnCl_2 \xrightarrow[-2CO_2]{2NO_2^+BF_4^-} \{[C_5H_4Mn(CO)_2NO]_2SnCl_2\}^{2+}(BF_4^-)_2 .$$

Nitroso-complexes are also formed on interaction of platinum group transition metals with NTFB[105,106]:

$$Ir(CO)Cl[P(C_6H_5)_3] + NO_2^+BF_4^- \rightarrow Ir(CO)(NO)Cl(BF_4)[P(C_6H_5)_3]_2 ;$$
$$RhCl[P(C_6H_5)_3]_3 + NO_2^+BF_4^- \rightarrow RhCl(NO_2)[P(C_6H_5)_3]_3^+BF_4^- .$$

The reduction of nitronium salts to NO^+ is also observed in the reaction of NTFB with nitrogen-containing iron(II) and cobalt(II) complexes[105].

IV. THE MECHANISM OF THE NITRATION OF AROMATIC COMPOUNDS

The range of studies devoted to the kinetics and mechanism of nitration by nitronium salts is fairly wide. They are all devoted to the nitration of aromatic hydrocarbons, but the absolute rates of reaction have been measured only for deactivated substrates containing nitro-groups in the aromatic ring, such as nitrobenzene[32,40,41], nitrotoluenes, 1,3-dinitrobenzene, and 2,4- and 2,6-dinitrotoluenes[41]. In these studies the nitration by nitronium salts was carried out mainly in acids (sulphuric, hydrofluoric, and methanesulphonic) and it was shown that nitration by nitronium salts in such media takes place analogously to nitration by nitric acid. The nitrating activity of nitronium salts solutions in acetonitrile[40] and nitromethane[41] is much higher than that of nitric acid.

Measurement of the absolute rates of nitration of benzene and alkylbenzenes by nitronium salts proved to be impossible even by the stopped flow method, because a sufficiently rapid way of arresting the reaction could not be found[107]. All the experiments on the nitration of benzene and alkylbenzenes were therefore carried out by the competitive method developed by Ingold[108,109].

Processes involving nitration by nitronium salts and nitric acid solutions differ most markedly as regards the rate of nitration of benzene and toluene. The ratio of the rates of nitration of toluene (K_t) and benzene (K_b) by nitric acid solutions is 25.[108,110] In competitive nitration by nitronium salts, the ratio $K_t/K_b = 1.67$ was obtained, approaching unity with increase of temperature from 25° to 55 °C (K_t/K_b = 1.13).[111] The relative rate depends also on the nature of the anion in the nitronium salt and on the solvent[47]. In the nitration of 4-methoxy-2,6-dimethyl-*N*-nitropyridinium tetrafluoroborate, $K_t/K_b = 44.5$.[48]

The sharp decrease of the sensitivity with respect to the nature of the substrate in nitration by nitronium salts (decrease of substrate selectivity) is apparently due to the increase of reactivity and the associated decrease of the directing influence of the substituent, i.e. the ratio of the *ortho*- and *para*-isomers formed in the nitration of toluene should approach the statistical value (2:1). This situation is observed, for example, in free-radical nitration by nitrogen dioxide, where a low substrate selectivity ($K_t/K_b = 2.6$) is accompanied, as was to be expected, by a decrease of the positional selectivity (37.2% of the *ortho*-isomer, 38.1% of the *meta*-isomer, and 24.7% of the *para*-isomer)[107].

The fundamentally novel feature of Olah's data for nitration by a nitronium salt was that, with a sharp decrease of substrate selectivity, the authors obtained almost the same ratio of the isomers as in nitration by nitric acid. These two results—decrease of substrate selectivity with retention of positional selectivity—were very difficult to reconcile.

Nowadays it has come to be believed that electrophilic substitution in aromatic compounds (including nitration by nitric acid solutions) proceeds via stages involving the formation of π- and σ-complexes[108,110,112,113]. Initially the π_1-complex is converted into the σ-complex, which is then converted into the π_2-complex and finally into the reaction product. The rate-limiting stage of the process is the formation of the σ-complex, which is particularly indicated by the correlation between the basicity of arenes (which determines the stability of the σ-complexes) and the rates of the electrophilic substitution reactions[110,113,114,115]. The energy profile of the reaction is presented in Fig. 1.

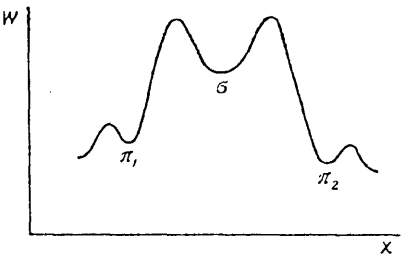


Figure 1. The energy profile of the electrophilic substitution reaction; W = energy; χ = reaction coordinate.

Olah observed that the rates of nitration by nitronium salts are better correlated with the stability of the π-complex[1,41,116,117], which led him and his co-workers to suggest that, in nitration by nitronium salts, the rate-determining stage is the formation of the π-complex and not the σ-complex (Fig. 2). This concept is extremely unusual for the theory of aromatic substitution.

Olah also believes that, in contrast to nitration by nitric acid solutions in which the π-complex arises on interaction with the electron system of the ring as a whole, nitronium salts form a directional π-complex where the nitronium cation is oriented towards the carbon atom with the maximum electron density. In the transformation of the π-complex into the internal σ-complex there is therefore no great energy expenditure and preferential *ortho–para* direction is achieved. The substrate selectivity in the nitration reaction is low, since the π-electron density in aromatic compounds depends little on the number of alkyl groups[112].

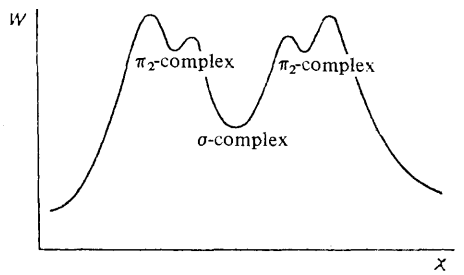


Figure 2. The energy profile of the reaction involving nitration by nitronium salts: $ArH + NO_2^+ \rightarrow ArNO_2 + H^+$; π_1-complex = $ArH...NO_2^+$; π_2-complex = $H^+...ArNO_2$; σ-complex = $ArHNO_2^+$.

Olah's interpretation of the experimental data has been criticised by a number of investigators[34,108,110,118–120]. Sikiguchi et al.[119] questioned the reliability of the ratios K_t/K_b obtained. They observed that in the competitive nitration of the benzene–toluene pair the ratio K_t/K_b depends on the dielectric constant ε of the solvent and changes from 2.15–2.31 for CCl_4 (ε = 2.23) to 16.3–19.7 for CH_3NO_2 (ε = 35), i.e. from a quantity close to that obtained by Olah to the usual values for nitric acid solutions. However, their study[119] nevertheless does not account for the low substrate selectivity in nitration by NTFB (also in nitromethane). Furthermore, their results[119] might have been influenced by the heterogeneity of the system, since nitric acid is very sparingly soluble in CCl_4 and aliphatic hydrocarbons.

Ritchie and Win[121] found that competitive nitration by NTFB in sulpholane caused different relative rates for binary (toluene–benzene) and quaternary (benzene–toluene–chlorobenzene–fluorobenzene) mixtures. They suggested that the nitration by nitronium salts is not fully kinetically controlled and that this might have been the cause of the "anomalous" results obtained by Olah and co-workers.

Doubts about the justification of the application of the competitive method to the study of the relative reactivities have been expressed by Tolgyesi[122], who showed, in relation to the nitration of the toluene–benzene pair by NTFB in sulpholane, that the ratio K_t/K_b increases with increase of the efficiency of mixing and the concentration of the hydrocarbons in solution and also with decrease of the NTFB concentration. Under certain conditions, the ratio K_t/K_b reaches 25–30, i.e. values corresponding to the reactivity in nitration by nitric acid solutions. However, it was shown later[107] that these results are due to the interaction of NTFB with the impurities present in the solvent.

In the nitration of durene (1,2,4,5-tetramethylbenzene) by solutions of nitronium hexafluorophosphate in nitromethane the yield of dinitrodurene was 8–10 times higher than that of mononitrodurene. On the other hand, under conditions of a more effective mixing of the reactants, mononitrodurene predominates[34]. These facts show that the reaction in essence occurs as soon as the components are mixed and that mass transfer processes therefore determine the reaction rate and the composition of the products. The nitration of pentamethylbenzene proceeds at a rate which is so high that the process is limited solely by the rate of mixing of the components[118,123]. The role of the mixing of the components has been confirmed by the nitration of bibenzyl in sulpholane. The main product of this reaction is the symmetrical dinitrobibenzyl even when there is a deficiency of the nitronium salt[124–126]. Thus the reactivity of NO_2^+ in nitronium salts is so high that the role of mass transfer increases sharply in the nitration process and to a greater extent the higher the reactivity of the substrate. Studies of the kinetics of the heterogeneous nitration of a number of substrates by NTFB using the "rotating disc" method[127] showed that, whereas the nitration of benzene takes place in the kinetic region, toluene is nitrated in the mixed region and the kinetics of the nitration of the still more reactive xylene and mesitylene are determined solely by diffusion processes. As was to be expected, the mass transfer conditions influence the substrate selectivity but not the positional selectivity[120,128,129].

Thus, in nitration by nitronium salts the concentration of the more reactive reactant at the site of mixing of the reactants diminishes so rapidly that the reactant cannot be supplied sufficiently rapidly by diffusion and the second reactant therefore reacts faster than would correspond to the ratio of the reactant concentrations, i.e. it is seemingly more reactive. This type of macroscopic diffusion effect can be eliminated in principle by rapid mixing and by employing a very low concentration of the more reactive substrate[110,122,126]. Furthermore, a second diffusion effect may appear in the system—a microscopic effect, whose essential feature is that the rate-determining process in the reaction becomes the collision of the reactants and not the formation of the reactive σ-complex. It has been shown[110,126,130–133] that the rate of nitration of alkylbenzenes by nitric acid in various media is limited by the number of encounters of the nitronium cation with the aromatic hydrocarbon, i.e. there is a limit to the reactivity of the substrate above which the introduction of activating substituents into the ring no longer increases the reaction rate. It is striking that, under conditions close to those corresponding to the maximum reaction rate, low substrate selectivities are obtained. The authors believe that, also in the case of very rapid nitration of alkylbenzenes by nitronium salts, the reaction rate is likewise limited by the rate of encounters with the substrate and this is why low substrate selectivities are obtained. Diffusion effects have been observed also in chlorination and bromination as well as nitration[134].

In later investigations[41,116,117] Olah admitted that the kinetics of the nitration of benzene and alkylbenzenes are determined by the encounter rate. Nevertheless he continues to believe that the mechanisms of the nitration of highly reactive compounds (benzene and alkylbenzenes) and deactivated substrates such as nitrobenzene and nitro- and dinitrotoluenes are different. An "early" transition state resembling an aromatic compound (a π-complex) is formed for highly reactive compounds. A low substrate selectivity (from 27 to 1) and a high (in the range 1–2) ratio of the *ortho*- and *para*-isomers are then usually observed. Relatively unreactive compounds (nitrobenzene, *o*- and *p*-nitrotoluenes, 2,4- and 2,6-dinitrotoluenes, etc.) give rise to

"late" transition states resembling a σ-complex. A high substrate selectivity is characteristic of such compounds (for example, the ratio of the rates of nitration of nitrotoluenes and nitrobenzene K_{nt}/K_{nb} is 100–500 and more for a low ratio of the *ortho*- and *para*-isomers (0.3–0.8).

According to Dewar[135,136] the "early" transition state retains aromatic properties to a considerable degree and is in many respects similar to an unperturbed aromatic system: the bond with the electrophile is still weak. The reaction with a strong electrophile is highly exothermic and one may therefore expect a relative stability of the intermediate and an appreciable difference between the latter and the transition state, which should be similar to the reactants in this instance according to Hammond's postulate[137]; the higher the reactivity of the electrophile, the smaller the influence of the substrate structure.

Schofield and co-workers reject Olah's concept of the "early" and "late" transition states[126,138] and, as already mentioned, explain the low substrate selectivity by the fact that the rate of nitration is limited by the diffusional process involving the formation of the "encounter complex" $ArH.NO_2^+$. The aromatic molecule as a whole and not just one carbon atom of the latter is involved in the formation of such a complex[126,130,138].

Stock[139] adheres to analogous views, believing that there are at present no data permitting the interpretation of Schofield's "encounter complex" as an oriented π-complex. He suggests the following mechanism of the nitration of aromatic compounds:

$$HNO_3 + H^+ \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} H_2O + NO_2^+ \ ;$$

$$NO_2^+ + ArH \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} ArHNO_2^+ \ ;$$

encounter complex

$$ArHNO_2^+ \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} + \text{(H, NO}_2\text{)} +$$

$$+ \text{(H, NO}_2\text{)} + B \xrightarrow{K_4} \text{(NO}_2\text{)} + BH^+ \ ;$$

B = base.

However, it has been noted[126] that the concept of the "encounter complex" which Schofield took from the diffusion theory, resembles somewhat Olah's concept of the "oriented π-complex". This became particularly apparent in a study[138] in which it was claimed that an intermediate preceding the σ-complex must be included in the nitration mechanism. The formation of such an intermediate, i.e. of the "encounter complex" is the rate-determining diffusion stage and the rearrangement of the complex to the σ-complex determines the composition of the products.

In his latest studies Olah[140,141] also assumes that the formation of the σ-complex is preceded by two stages:

$$RC_6H_5 + NO_2^+ \overset{\text{stage 1}}{\rightleftharpoons} [RC_6H_5NO_2]^+ \overset{\text{stage 2}}{\rightleftharpoons} \underset{\text{(LVIII)}}{RC_6^+H_4\text{(H, NO}_2\text{)}} \overset{\text{stage 3}}{\xrightarrow{-H^+}} RC_6H_4NO_2 \ .$$

Stage *1* determines the overall rate of reaction and is responsible for the substrate selectivity, while stage *2* is responsible for the positional selectivity, i.e. the proportions of the isomers in nitration. The author explains by the presence of these two stages the high positional selectivity accompanied by a very low substrate selectivity in the nitration of highly reactive aromatic hydrocarbons by nitronium salts. The nature of the intermediate (LVIII) has been elucidated and Olah believes that this can be a π-complex, Schofield's "encounter complex", or even a radical pair of NO_2 and ArH^+, whose existence has been postulated for aromatic hydrocarbons with a high electron density[144]. The closeness of Olah's and Schofield's views is evident.

The question of the position of the transition state on the reaction coordinate, i.e. the determination of the stage responsible for the formation of a π- or σ-complex in nitration by nitronium salts, is more complex. The differences between Olah and Schofield as regards this question arise apparently from the different interpretations of the Hammett equation and Hammond's postulate. Johnson and Schofield[143,144] believe that it is quite inadmissible to employ the reaction constant as a characteristic of the selectivity–reactivity relation derived from Hammond's postulate. The large variations in selectivity found by Olah are a consequence of the inaccuracy of the competitive method for high reaction rates. Johnson[144] notes that the principle of selectivity implies the validity of the isokinetic relation, but the proportionality between the enthalpy and free energy by no means always holds. In many instances Hammonds postulate is invalid, i.e. one cannot regard as valid the hypothesis that the reaction constant ρ always reflects exactly the character of the transition state. The author believes that Hammond's postulate is insufficiently justified for electrophilic substitution reactions and that the conclusions usually associated with the values of ρ determined from the Hammett equation are exactly the opposite of those which follow from Hammond's postulate. If an attempt is made to determine the nature of the transition state for a given reaction with the aid of the Hammett equation on the basis of the different reaction rates in the presence of different substituents, then it follows from Hammond's postulate that the character of the transition state itself varies with the rate of the process.

Evidently a more detailed description of the conflict in the interpretation of the Hammett equation and Hammond's postulate is outside the framework of the present review.

New conclusions and the controversy concerning the nitration reaction and other electrophilic aromatic substitution reactions, whose mechanism appeared to be rigorously proved and understood after the publication of Ingold's book[108], have shown that studies in this field must be continued and that the treatment and interpretation of experimental data must be particularly thorough with allowance for diffusion processes.

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Structural Chemistry of Hydrides of Intermetallic Compounds

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The contemporary state of the structural chemistry of the hydrides of intermetallic compounds is discussed. X-ray and neutron diffraction data on hydride phases are surveyed and critically analysed. Tetrahedral and octahedral coordination are shown to be most typical for hydrogen atoms in the structures of multi-component hydride phases. Rules for the structure of intermetallic hydrides are formulated, permitting us to forecast the structures of compounds not yet studied and to predict the maximum capability of the parent intermetallic compounds to absorb hydrogen. 204 references are given.

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I. INTRODUCTION

Compounds of hydrogen with metals are of great interest for the solution of practical and theoretical problems in the new field of science, atom–hydrogen energetics. Metal hydrides can be considered as effective chemical storage and sources of hydrogen, but only if the reaction of hydrogen with the metal in question occurs rapidly and with sufficient completeness under comparatively mild conditions, and the hydrogen weight content in the hydride proves to be high enough.

At pressures up to several kilobars molecular hydrogen reacts only with the limited number of metals which have low ionisation energies: the alkali, alkaline-earth, and lanthanide metals. Titanium, vanadium, and zirconium approach these in respect of their reactivity with hydrogen. It is only recently that a number of unstable hydrides of the transition metals Mn, Fe, Co, Mo, and Rh have been obtained under high pressure conditions[1-5].

However the preparation of hydrides by direct reaction of hydrogen with the metal is not always easily realisable in practice. In the majority of cases the kinetics of absorption and desorption of hydrogen are very sensitive to the presence of minor impurities in both the hydrogen and the metal, the "absorption $\rightleftharpoons$ desorption" equilibrium is established slowly even at relatively high temperatures (300–400 °C), and products with a high content of the primary substance are obtained only in isolated cases.

This is why such great interest was aroused by the discovery at the end of the 1960's of a new type of reaction between hydrogen and intermetallic compounds (IMC) and alloys, one of whose components is a metal capable of forming a stable binary hydride. Chance observations made almost simultaneously by various independent research groups opened up a

new chapter in the chemistry of metal–hydrogen compounds. Their work showed that many IMC's containing Ti, lanthanides (Ln), or Mg react readily with hydrogen at 25–100 °C under 0.1 to 100 atm pressure. The kinetics of this reaction are unique and have no analogy in the chemistry of binary hydrides—the absorption of hydrogen by the metallic phase begins almost immediately and close to room temperature the "absorption ⇌ desorption" equilibrium is as a rule established in a few minutes, depending on the nature of the metallic phase and the purity of its surface.

Up to the present there have been about 500 publications devoted to study of the reaction of various IMC's and alloys with hydrogen. A large amount of experimental data, of interest not only to chemistry but also to those areas of physics, technological and applied sciences bordering on chemistry, has been accumulated. However the structural chemistry of the hydrides remains relatively unstudied—as regards both strictly structural research, little of which was carried out until recently, and also work on the nature of the metal–hydrogen chemical bond.

Finally, structural investigations based on the application of diffraction methods cannot give direct information on the valence state of hydrogen in its compounds with metals, but they are necessary for the development of descriptive crystal chemistry of metal hydrides and they can be very useful (as we have remarked repeatedly) for solving certain definite practical problems connected with the prediction of and search for new polymetallic compositions which absorb a large quantity of hydrogen reversibly at given temperatures and pressures.

The purpose of this review is to discuss the structural chemistry of hydrides containing two or more metal components. Questions of the crystal chemistry and structure of binary hydrides are considered only in so far as they are necessary for the analysis of general rules determining the structure of both binary and more complex hydride phases. We were aware also that substantial reviews of work on the structure of binary metal hydrides have previously been published by Mueller et al.[6], Goldschmidt[7], Mackay[8], Libowitz[9], Stalinski[10], Galaktionova[11], and Andrievskii and Umanskii[12].

II. THE STRUCTURE OF BINARY METAL HYDRIDES

The descriptive crystal chemistry of metal hydrides can be based on the idea that they are unusual "interstitial phases" of hydrogen in a metal lattice-matrix. The alternative view, according to which metal hydrides are regarded as ionic compounds M^+H^-, does not in the majority of cases correspond[12] to the actually observed picture of the structure and physical properties of the hydrides of metals of groups III–VIII.

Analysis of structural relationships in binary hydrides shows that insertion of hydrogen into the metal lattice can occur in two ways:

(1) it is accompanied by a fundamental reorganisation of the metal lattice or in other words by a change in the type of packing of the metal atoms, e.g. by a transition from body-centred cubic (b.c.c.) packing in the structure of the metal itself to face-centred cubic (f.c.c.) packing in the metal sublattice of the hydride; or

(2) it does not lead to a substantial change in the metal structure—in this case the packing of the metal atoms in the metal sublattice of the hydride is no different from the packing in the structure of the metal itself or only an insignificant deformation of the unit cell occurs.

The overwhelming majority of metals react with hydrogen in the first way. It is only for such elements as V, Ni, Nb, Pd, Ta, Ce, and Th that the unit cells of the hydride phases have a simple relationship to or match the original unit cells of the metals.

The hydrogen atoms in the binary metal hydride structures have three types of coordination polyhedra: tetrahedra, octahedra, and triangles. The largest size holes, the octahedral holes in the f.c.c. and the hexagonal close packed (h.c.p.) lattices, are the first to be filled by hydrogen atoms in the structures of hydrides of elements with small atomic radii (metals of groups VI–VIII). However, on passing to the lanthanides, which have considerably larger atomic radii, the tetrahedral holes are filled first and only after that the octahedral. It is only in the structures of HoD_3,[13] YD_3,[14] and Th_4D_{15} [15] that the deuterium atoms have a triangle form of coordination polyhedron.

Thus the general rule of crystal chemistry, that the coordination number (c.n.) of an atom M′ falls as the atomic radius ratio $r_M/r_{M'}$† (r_M/r_H in the present case) increases, is obeyed also in the metal hydride structures—the c.n. of the hydrogen atom changes from 6 to 4 or to 3 as the metal radius increases.

If the M–H(D) interatomic distances in the binary hydride structures are taken to be the sum of the atomic radius of the metal M and the effective radius of the hydrogen atom, it is possible to form a qualitative estimate of the latter#.

It is known that in interstitial structures the size of the holes in the lattice matrix, made up of atoms of radius r_M, increases in the sequence: triangular (c.n. =3; $r_{hole} = 0.22\, r_M$) < tetrahedral (c.n. = 4; $r_{hole} = 0.41\, r_M$) < octahedral (c.n. = 6; $r_{hole} = 0.73\, r_M$).[17] This implies that the radius of the hydrogen atoms, which occupy various types of hole, cannot generally speaking be constant but depends markedly on the type of environment. It is also clear that this effect will be more marked the more complex is the structure of the parent matrix, of metal or an IMC.

These rules are followed in the binary metal hydride structures. The hydrogen atoms with the "largest radius" are those in octahedral holes, their size decreasing with decrease in the metal atom dimensions from 0.7–0.8 Å in lanthanum and cerium hydrides to ~0.6 Å in the hydrides of the metals of groups VI–VIII. The hydrogen atoms with a c.n. of 3 in the $ScH_{2.65}$ structure[18] have the smallest radius (~0.3 Å); this is close to the covalent radius of hydrogen, 0.28 Å.[8] Hydrogen atoms occupying tetrahedral holes have radii in between the values for c.n. 3 and c.n. 6 (0.4–0.5 Å).

The H–H interatomic distances in the structures of binary hydrides of metals of groups VI–VIII are fairly large owing to the low density of hydrogen nuclei in them (~2.6 Å). However, on increasing the hydrogen content in the hydride phases the smallest H–H distances are reduced considerably (to ~2.1 Å in the lanthanide trihydrides and even to ~1.9 Å in the $ScH_{2.65}$ structure).

In conclusion we note a characteristic feature of binary hydride structures: notwithstanding that in the f.c.c. and h.c.p. structures the holes occupied by hydrogen atoms are regular polyhedra, these atoms do not always lie exactly in the centres of the holes. In the hexagonal hydride structures MH_3 and also in $CeD_{2.29}$ [19] the hydrogen atoms are displaced from the centres of both the tetrahedral and octahedral holes, and in the HoD_3 structure this displacement from

†M denotes the element whose atoms have the larger radius and M′ the smaller.

#Values for the metal radii were taken from Pearson[16].

the octahedron centre is so marked that the c.n. of the hydrogen atom becomes equal to 3. The structures of $CeD_{2.51}$ [20] and LaD_3 [21] are particularly representative in this respect; in these, in addition to the shift of the hydrogen atoms from the centres of the octahedral holes, a feature typical of the crystal chemistry of metal hydrides is exhibited: statistical occupation by the hydrogen atoms of a fraction of the crystallographic equivalent positions in the hydride phase structure.

III. GENERAL RULES OF THE REACTION OF HYDROGEN WITH INTERMETALLIC COMPOUNDS

Hydride phases, containing two or more metal components, can be obtained either by hydrogenation of alloys or IMC's of the composition $M_nM'_m$ or by high-temperature synthesis from the binary hydride of one metal and a second metal in an atmosphere of hydrogen. In the latter case a hydride phase $M_nM'_mH_x$ is formed, whereas in the former case three types of reaction are possible[22–24] (the first two of these correspond entirely to the schemes described above for the reaction of individual metals with hydrogen).

1. A compound with a new type of structure is formed.
2. The intermetallic compound absorbs a significant quantity of hydrogen without a substantial deformation of the original crystal structure.
3. There is complete decomposition of the initial IMC and formation of a stable binary hydride MH_x and an intermetallic compound enriched in the metal M′ which is inactive towards hydrogen, with the composition $M_{n-y}M'_m$ (or a hydride phase based on this), or of the metal M′ directly—a hydrogenolysis reaction[23].

The hydrogenolysis reaction of intermetallic compounds does not come within the scope of this review. Therefore the crystal chemistry of the phases formed only by the first or second mechanisms is discussed.

Before proceeding to examine the structural relationships between the IMC and the hydride phases based on them an important feature of IMC structure should be noted. In contrast to the structure of pure metals, in which all the interatomic distances within the range of the closest coordination sphere are as a rule identical, a greater diversity is observed in an IMC—there are distances both shorter and longer than the sum of the respective metal radii, and the variations may be considerable. It will further be shown

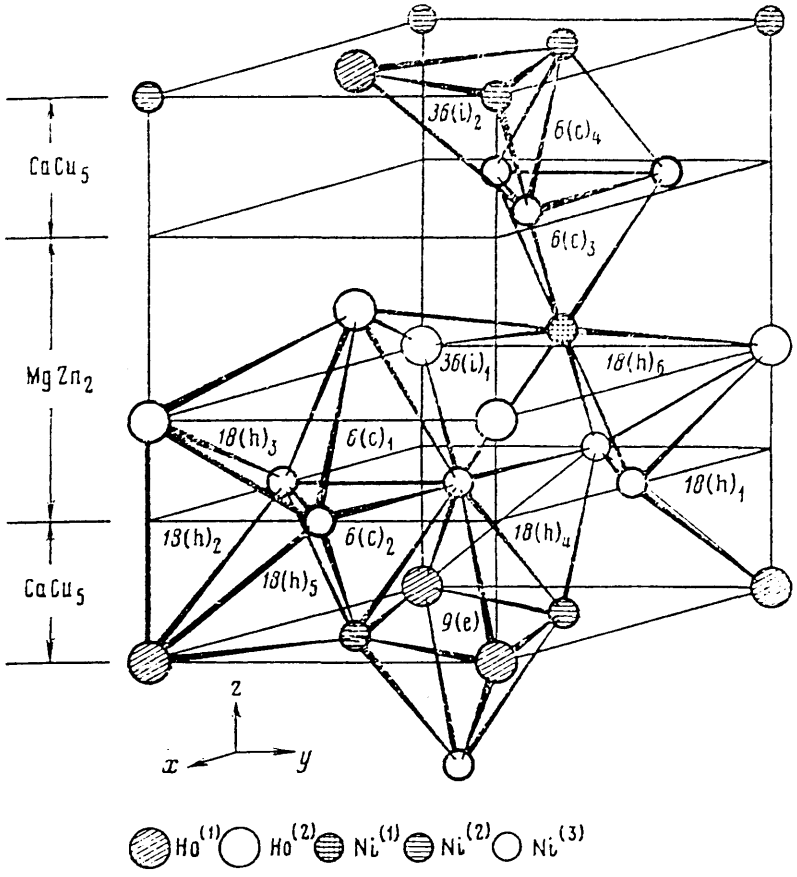


Figure 1. Holes in the $HoNi_3$ structure[40] (the part of the unit cell with $z = 0–1/3$ is shown); the $CaCu_5$ and $MgZn_2$ type sections are marked. The holes (13 different types) are designated by symbols (number of positions and Wyckoff notation) for the equivalent positions in the space group $R\bar{3}m$ corresponding to the centres of the holes.

that the insertion of hydrogen atoms takes place preferentially in those holes whose periphery includes precisely those "long", most easily deformed bonds.

A principal feature of the reaction of IMC's with hydrogen is that, in contrast to metals, in the overwhelming majority of cases the IMC structures do not undergo serious reorganisation on hydrogenation, and the mutual arrangement of the metal atoms in the structure of the hydride phase remains the same, or almost the same, as in the parent IMC.

The structure of hydride phases based on IMC's with structures of the $CaCu_5$, $MgCu_2$ and $MgZn_2$ (Laves phases), $PuNi_3$, Ce_2Ni_7, Gd_2Co_7, Th_6Mn_{23}, Ti_2Ni and CrB types have been investigated most fully. Note that the first six structure types are related and are members of one homologous series of structures MM'_5–MM'_2.[16,25,26] The structures of compounds with a composition intermediate between MM'_5 and MM'_2 can be regarded as consisting of fragments of the $CaCu_5$ and Laves phase type structures. The superposition of these fragments occurs along the [001] direction of the hexagonal unit cell owing to the presence of identical planar nets in the Laves phase and $CaCu_5$ structures. For example, the $PuNi_3$ type structure can be obtained by successively placing one above the other a $CaCu_5$ type unit cell and half of an $MgZn_2$ type unit cell (see Fig.1). As will be shown below, the homologous relationship of these structures predetermines also the similar nature of their reaction with hydrogen.

The hydride phases based on the intermetallic compounds $LaNi_5$ and $CaNi_5$, and also on the alloys $ThNi_3Al_2$, MNi_4Al (M = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho), $MNi_{5-x}M'_x$, where M' = Al, Cr, Fe, Cu,[27–30] retain the hexagonal symmetry of the original MM'_5 structures of the $CaCu_5$ type and the unit cell expands on their formation to an equal extent both in the basal plane and in the [001] direction. Some other structure is evidently possessed by the hydride phases based on the alloys $LaNi_{5-x}Co_x$ (x = 0.5–3.0) because the increase in the unit cell volume occurs mainly through an increase in the lattice parameter a, while the change in the c parameter is insignificant[31].

The hydride phases MCo_5H_x have orthorhombic unit cells which are produced from the original MCo_5 structure by an anisotropic expansion in the basal plane of the hexagonal unit cell with a negligible change in the c parameter[27]. $LaCo_5$ absorbs the largest quantity of hydrogen ($H/LaCo_5$ = 4.3).§ In the γ-hydride so formed the lattice parameter ratio $a/b\sqrt{3} < 1$, in contrast to the hydride phases with $H/MCo_5 < 4$, the so-called β′-, β″-, and β‴-hydrides, for which $a/b\sqrt{3} > 1$.[27] In the β″- and β‴-hydride structures the c parameter is doubled, as indicated in the case of the β‴-hydride by neutron diffraction data. Studies of hydride phases based on alloys of the $La_{1-x}Pr_xCo_5$, $Ce_{1-x}Pr_xCo_5$ and $La_{1-x}Ce_xCo_5$ systems showed[33,34] that they have the β-hydride structure with a doubled c parameter.

The reaction of hydrogen with IMC's of the MM'_2 composition with Laves phase structures, where M is Sc, Y, Ta, Th, a lanthanide, or a Group IV metal and M′ is a transition metal from either period IV or V, has been investigated[30,35–68].

The unit cells retain the original hexagonal symmetry in all cases of hydride phases based on IMC's with the $MgZn_2$ type structure containing Ti, Zr, Er, Lu, and Th as the M component, and also in $ScFe_2$ crystallised with the $MgNi_2$ type structure[30,35–48].

IMC's with $MgCu_2$ type structures react differently with hydrogen. Although in the majority of cases there is an isotropic expansion of the unit cells without a change in their f.c.c. symmetry, for some hydrides of the MM'_2H_x type it was established that there are three different modes of deformation of the original unit cell, leading to unit cells which are primitive cubic with a doubled a parameter[61], orthorhombic with $a \sim b \sim a_{cubic}/\sqrt{2}$ and $c \sim c_{cubic}$,[49,50,54,61] or rhombohedral[66].

With a gradual change in the hydrogen content in the phases ZrV_2H_x and $ZrCr_2H_x$ from $x \sim 0$ up to saturated hydrides the structure of the matrix does not change, but the unit-cell parameters are increased[35]. Analogous results were obtained for YMn_2H_x.[60]

Hydrogenation of MM'_5 compounds (M = lanthanide, Y, Ca) with $PuNi_3$ type structures, when M′ is Co or Ni, leads to formation of di- and tetra-hydride phases and is not accompanied by a change from the symmetry of the original rhombohedral lattices[55,56,68–73]. When hydrogen is absorbed by the intermetallic compound up to the H_2-phase composition there is an expansion of the lattice matrix in the [001] direction of the trigonal unit cell with a negligible change in the a parameter. In the tetrahydride phases, in contrast to the dihydrides, the parameter a increases markedly, i.e. a further increase in the unit cell volume occurs as a result of expansion in the basal plane. When M′ = Fe only one hydride phase, similar to the phase $MCo(Ni)_3H_{\sim 4}$ in composition and crystallographic characteristics, is formed[71,72].

Also, on exceeding a certain critical temperature, below which a two-phase region of α-solid solution and saturated hydride exists, the hydride phases MFe_3H_x (M = Dy, Er)[74–76] acquire the characteristics of a solid solution: a change in their hydrogen content is accompanied by a continuous increase in the unit-cell dimensions.

The data[77] on the existence of the mono- and di-hydrides $DyCo_3H_{1.0}$ and $DyCo_3H_{1.8}$, whose unit cells are "contracted" in the z axis direction as compared to the $DyCo_3$ structure, evidently require experimental verification, since they are not in agreement with other results[70–72].

The $CeCo_3$–H_2 system, in which only one hydride phase $CeCo_3H_3$ is formed, occupies a special place amongst MCo_3–H_2 systems. This phase is analogous in crystallographic characteristics to H_2-phases but the increase in its c parameter is anomalously large, amounting to 32%,[56,72] which is 3–5 times greater than in the dihydrides $MCo(Ni)_3H_{\sim 2}$.

The intermetallic compound $CeNi_3$ which crystallises in an analogous structural type reacts with hydrogen in a similar way—only one hydride phase, $CeNi_3H_3$, is formed and then only the c lattice parameter is substantially increased[56].

Hydrogenation of IMC's of composition M_2Co_7 with the Ce_2Ni_7 and Gd_2Co_7 type structures leads in both cases to formation of two hydride phases $M_2Co_7H_{\sim 3}$ and $M_2Co_7H_{\sim 6}$, but whereas the transition from α-solution to the hydride phase $M_2Co_7H_{\sim 3}$ is accompanied by expansion of the hexagonal (or trigonal) unit cells only in the z axis direction, when the hydride phase $M_2Co_7H_{\sim 6}$ is formed the a parameter increases[56,72].

The hydride phases Ti_2NiH_x (x = 0.5, 1.0, 2.0, 2.5) have been interpreted as individual compounds[78]. However there is no change in the structure of the metal matrix on hydrogenation—the cubic structures of these phases merely have enlarged unit-cell parameters as compared to the original intermetallic compound Ti_2Ni (which crystallises in an analogous structure type). On hydrogenation of the alloys $Ti_2Co_{1-x}Fe_x$,[79] $Ti_2Ni_{1-x}Fe_x$,[80] $Ti_2Ni_{1-x}Co_x$,[80] and the compounds Hf_2M' (M′ = Co, Fe, Mn, Rh),[81,82] which have the same type of structure as Ti_2Ni, the volume of the unit cells of the original structures increases but their cubic symmetry does not change.

The compounds Ti_2Ni, Ti_2Cu, Ti_2Fe, and Ti_2Co are able to absorb oxygen without a change in the initial structure up to the composition $Ti_2M'O_{0.5}$.[83–86] Hydrogenation of the oxygen-containing phases leads to mixed oxyhydride phases whose structures also possess the original cubic symmetry[83–86].

§ With a high pressure of hydrogen (up to 1400 atm) the phase $LaCo_5H_9$ is formed[32].

Judging from neutron-diffraction data[87], several hydride phases are formed on hydrogenation of the intermetallic compound Y_6Mn_{23} with the complex cubic structure of the Th_6Mn_{23} type. The move to phases richer in hydrogen is accompanied by a gradual increase in the volume of the cubic unit cells. However, in most of the work the values of the unit-cell parameters are quoted only for the hydride phases richest in hydrogen[56,57,68,88,89].

The hydride phases based on IMC's with structures of the types CrB ($ZrNiH$,[90] $ZrNiH_3$ [91]), ZrAg ($ZrAgH$ [92]), Th_7Fe_3 ($Th_7Fe_3H_{14.2}$ [93]), $CuAl_2$ (Hf_2NiH_3 [82], Th_2AlD_4 [94]), UNi_5 ($YNi_4.MnH_{4.5}$ [95]), $CeCo_4B$ ($CaNi_4BH_{4.5}$ [55]), CsCl [$TiFeH(D)$,[96,97] $TiFeD_{1.9}$ [98]], Zr_4Al_3 ($Zr_4Al_3H_{4.3}$ [99]), $MoSi_2$ ($Hf_2CuH_{2.8}$, $Ti_2PdH_{2.0}$, $Zr_2PdH_{2.7}$, $Hf_2PdH_{1.9}$ [100]), and Cr_3Si ($V_3GaH_{2.0}$ [101]) also have structures whose unit cells either correspond to the unit cells of the parent IMC structures or are derived from them. In contrast to these, the hydride phases based on the intermetallic compounds TiNi,[78] Mg_2Ni,[102,103] Zr_2Cu,[100] HfCo,[82] HfNi,[82], ZrCo,[104] Ti_3Al,[105] and TiCo [106] have crystal structures whose unit cells are not simply related to those of the parent IMC structures.

The structure of hydride phases obtained by high-temperature synthesis at low hydrogen pressures (~1 atm) from a mixture of the binary hydride of a metal M and a metal M′ have been studied[107–116]. The phases formed are $M_2M'H_{4-6}$ (M = Ca, Sr, Eu, Yb; M′ = Ru, Rh, Ir),[107,108,112,114,115] Sr_2PdH,[110] Sr_2PdH_4 and $Ca_3Pd_2H_4$ [111] with cubic structures and also Li_4RhH_4 and Li_4RhH_5,[116] whose structures possess tetragonal and orthorhombic symmetry respectively; from a mixture of two binary hydrides the phases $LiEuH_3$,[109] $LiBaH_3$ and $LiSrH_3$ [110] with antiperovskite type structures are formed. Saturation of the alloys $ThZr_2$ and $ThTi_2$ with hydrogen at elevated temperatures leads to formation of the phases $ThZr_2H_7$ and $ThTi_2H_6$ and it is accompanied by ordering of the metal atom arrangement as in the Laves phases $MgZn_2$ and $MgCu_2$.[113]

The formation of hydride phases richest in hydrogen leads to a 20–25% increase in the unit-cell volume of the IMC structures, although for a number of structures the ratio $\Delta V/V_0$ exceeds this amount by almost a factor of two (approximately 37% for hydrides based on $CeRu_2$ [143] and $ThMn_2$ [42]). The ratio of the change in the IMC unit-cell volume on hydrogenation ΔV to the number of absorbed hydrogen atoms is close to 2.5–3.5 Å^3 for all the hydride phases studied.

Li_4RhH_4 and Li_4RhH_5 are representative of a few metal hydrides for which an X-ray structure examination has been carried out on single-crystal specimens[116]. In Li_4RhH_4 the c.n. of the hydrogen atom is 6 and its coordination sphere comprises one Rh and five Li atoms forming a distorted octahedron. The structure needs refining by neutron diffraction. The structure of Li_4RhH_5 was not determined so reliably, the positions of all the atoms being deduced from geometrical considerations and from the relationship between the Li_4RhH_4 and Li_4RhH_5 structures.

As a rule, X-ray powder diffraction investigations of the structure of hydride phases do not make it possible to determine the positions in the crystal lattice occupied by hydrogen atoms. To solve this problem it is necessary to use neutron diffraction.

IV. CRYSTAL-CHEMICAL ANALYSIS OF THE STRUCTURES OF INTERMETALLIC COMPOUNDS AS MATRICES FOR THE ADSORPTION OF HYDROGEN

As hydride phases based on IMC's are as a rule powders in which the individual grains are not large enough for them to be used for single-crystal structure determination, neutron powder diffraction has up to the present been used in all the work carried out. The absence of single-crystal specimens creates certain difficulties for the solution of the structure—the traditional methods of structure analysis can be used only in isolated favourable cases to obtain results from a powder diffraction experiment owing to the limited number and overlapping of the reflections in the diffraction pattern. The method of line profile analysis[117] has considerably widened the possibilities of neutron powder diffraction analysis; however its use does not of course enable us to overcome the principal deficiencies of the powder experiment mentioned. The only possible method for solving the structure from the neutron powder diffraction data is to show that there is agreement between the intensities of the reflections calculated theoretically for the proposed model of the structure and those measured experimentally. Since the positions of the metal atoms in the hydride phase structures are close to their positions in the original IMC, the problem becomes one of determining the positions occupied by the hydrogen atoms on entry into the metal lattice.

The principles for constructing the most probable models for the structure of hydride phases based on IMC's can be formulated in the following way[30,40,118].

1. The positions in the parent metal lattice most preferable for filling with hydrogen atoms are the tetrahedral holes with a radius $\geqslant$0.4 Å.

2. The M–H interatomic distances in the IMC hydride lattice are similar to those in the binary hydride lattices; the minimum permissible value is equal to the sum r_M + (0.2 to 0.3) Å.

3. The H–H interatomic distances must not be substantially less than 1.8–2.0 Å.

In addition the following hypotheses are very important when analysing a model for the structure:

4. The preferable holes for occupation are those surrounded to a maximum extent by atoms of the metal M which is more active towards hydrogen (capable of forming a stable binary hydride).

5. The greater the M–M distances between the atoms making up the hypothetical coordination polyhedron in comparison to the sum of the corresponding metal radii, the more easily is this polyhedron deformed and hence the more easily is a hydrogen atom inserted in the hole.

The last hypothesis was put forward *a priori* in 1979 [119] and has been confirmed by an analysis of experimental results obtained over the last three years.

An analysis of possible models for the structures of hydride phases based on IMC's has been carried out, using the hypotheses set out above, for the structure types $CaCu_5$ (on the example $LaNi_5$),[118] $MgCu_2$ (example $ZrCr_2$),[120,121] $MgZn_2$ (example ZrMoFe),[40,121] $PuNi_3$ (example $HoNi_3$),[70] Th_6Mn_{23} (example Y_6Mn_{23}),[87] CrB (examples ZrNi and LaNi),[122–124] and for some other types. Considering that at the present time the structure of the majority of the corresponding hydrides (or deuterides) is already established by neutron diffraction, a detailed account of the results obtained is hardly necessary and so we restrict ourselves to an enumeration of the most characteristic features of the models for the structures of the hydrides of intermetallic compounds which distinguish them from the structures of binary metal hydrides. The main difference is that, as already noted, the number of different types of hole in IMC structures as a rule significantly exceeds the corresponding number in binary hydride structures. Thus, in the $CaCu_5$ type structure there are 5 types of hole suitable in principle for filling by hydrogen atoms[118], in the $MgZn_2$ structure 7 types[40,121], in the Th_6Mn_{23} structure 9 types[87], in the CrB structure 7 types[124], and in the $PuNi_3$ structure (Fig.1) as many as 13 types[70]. The

second, and no less important, difference is that in IMC structures three groups of hole can be distinguished according to the metal atoms surrounding them: (a) holes formed only by atoms of the metal M; (b) holes formed only by atoms of the metal M'; (c) holes with mixed surroundings (metals M and M'), whereas in the binary hydride structures the holes cannot of course be divided into different groups on this basis.

The analysis has shown that insertion of hydrogen atoms in the tetrahedral holes¶ [hM'_4] of the parent IMC structures is least probable because, firstly, they are smallest in size and, secondly, they are formed by atoms of the metals M' which are inactive towards hydrogen (nickel, chromium, manganese, molybdenum, or iron). In addition, the M'–M' interatomic distances on the periphery of these holes are as a rule less than double the radius of metal M', so making filling of the holes difficult.

Table 1. Characteristics of the types of hole most preferred for introduction of hydrogen atoms into the structures of $LaNi_5$,[118] $ZrCr_2$,[120] ZrMoFe,[30] $HoNi_3$,[30] Y_6Mn_{23},[87] and LaNi [163] (r is the effective radius of the hole).

Structure	Type of hole	Interatomic distances, A*			Coordinates**			r, Å	n***
		M – M	M – M'	M'–M'	10^3x	10^3y	10^3z		
$LaNi_5$	[hLa_2Ni_2]	3.98	4 at 3.20	2.51	107	214	500	0.51	1/2
$ZrCr_2$	[hZr_2Cr_2]	3.12	4 at 2.99	2.55	815	815	131	0.38	1/2
ZrMoFe	[hZr_2(Mo, Fe)$_2$]	3.17	4 at 3.03	2.59	463	926	250	0.39	1
	[hZr_2(Mo, Fe)$_2$]	3.17	4 at 3.03	2.59	240	480	250	0.39	1
	[hZr_2(Mo, Fe)$_2$]	3.17	2 at 3.03; 2 at 3.04	2.59	544	88	130	0.39	1
	[hZr_2(Mo, Fe)$_2$]	3.17	3 at 3.03; 3.04	2.59	283	327	934	0.39	1/2
$HoNi_3$	[hHo_2Ni_2]	3.42	2 at 2.85; 2 at 3.19	2.48	125	249	73	0.42	1
	[hHo_2Ni_2]	3.42	2 at 2.85; 2 at 3.19	2.48	875	750	73	0.42	1
Y_6Mn_{23}	[hY_6]	6 at 2.54	—	—	0	0	0	0.74	1
LaNi	[hLa_3Ni_2]	2 at 3.69; 4.36	2 at 2.93; 4 at 2.99	3.81	0	925	250	0.45	1

*According to published data[16], the metal radii (in Å) (for c.n.$_M$ = 12) are as follows: r_{La} = 1.877, r_{Ni} = 1.246, r_{Ho} = 1.766, r_{Zr} = 1.602, r_{Cr} = 1.282, r_{Mo} = 1.400, r_{Fe} = 1.274, r_Y = 1.801.

**Data on the metal atom arrangement in the structures of the parent intermetallic compounds are given in refs. 30, 87, 118, 120, and 163.

***n is the maximum possible occupation factor of the holes under the condition $d_{h\text{-}h} \geqslant 1.8\text{–}2.0$ Å.

¶In this article the method adopted by Soviet authors (see, for example, Kripyakevich's monograph[25]) is used to signify holes (h) and coordination polyhedra of atoms: following specification of a hole or the central atom of the polyhedron (in this article D or H) the metal atoms forming the hole or coordination polyhedron are stated in decreasing order of their radii.

The holes in the parent IMC structures most preferred for filling by hydrogen atoms are the largest: the tetrahedral [$hM_2M'_2$] ($LaNi_5$, $ZrCr_2$, ZrMoFe, and $HoNi_3$ structures), the octahedral [hM_6] (Y_6Mn_{23} structure) and the hole of form [$hM_3M'_2$] at the centre of a trigonal bipyramid (LaNi and ZrNi stuctures), because their periphery involves a high proportion of atoms of the metal M which is active towards hydrogen (Y, Zr, La, Ho) as compared to other holes. In addition, filling of these holes by hydrogen atoms is favoured by the fact that their periphery contains a larger number of M–M distances which exceed the sum of the corresponding metal radii than do other types of hole. The basic data describing the types of hole listed above are given in Table 1.

In the structures under consideration the tetrahedral holes [hMM'_3] ($LaNi_5$, $ZrCr_2$, ZrMoFe, $HoNi_3$, and Y_6Mn_{23} structures), [$hM_2M'_2$] (Y_6Mn_{23}, LaNi, and ZrNi structures), [hM_3M'] (LaNi and ZrNi structures), and the octahedral holes [$hM_2M'_4$] ($LaNi_5$ and $HoNi_3$ structures) can also be singled out. If we take into account the dimensions of these holes, the nature of their periphery, and the magnitudes of the distances between the metal atoms forming the holes, we see that they are less likely to be filled than the holes listed in Table 1; however it is quite possible that hydrogen atoms are placed simultaneously in the most preferred holes (see Table 1) and in these latter holes [hMM'_3], [$hM_2M'_2$], [hM_3M'], and [$hM_2M'_4$] in hydride phase structures.

The specified hypotheses on the principles for setting up models for the structures of hydride phases have been confirmed by neutron-diffraction studies.

V. NEUTRON-DIFFRACTION STUDIES OF THE CRYSTAL STRUCTURES OF THE HYDRIDE PHASES $M_nM'_mH(D)_x$

The largest number of hydride structure investigations published up to the present are of those based on IMC's with the hexagonal structure of the $CaCu_5$ type[27,40,118,125–134]. Although the introduction of hydrogen into the MM'_5 lattice leads to a different deformation of the unit cells in nickel-containing ($LaNi_5D_{6.0}$, $LaNi_4AlD_{4.1}$, etc.) and cobalt-containing ($CeCo_5D_{2.55}$, $PrCo_5D_{3.6}$) hydrides (or deuterides) (see Table 2), all these structures are related to each other and are different versions of the model for the structure of the phase $MM'_5H(D)_x$, in which the tetrahedral holes [$hM_2M'_2$] and [hMM'_3] (or the octahedral holes [$hM_2M'_4$]) of the parent IMC lattice are filled. The most substantial differences between the $MNi_{5-y}Al_yD_x$ structures and the MCo_5D_x structures are connected with some displacement of the deuterium atoms from the layers of metal atoms, situated in planes perpendicular to the z axis, since in the MCo_5D_x structures the deuterium atoms are in the planes of these layers (see Figs. 2 and 3). These displacements lead to a change in the form of the coordination polyhedron and the c.n. of the deuterium atoms from 6 in the octahedral [$hM_2M'_4$] holes of the MCo_5D_x structures to 4 in the tetrahedral [hMM'_3] holes of the $LaNi_5D_{6.0}$ and $LaNi_4AlD_{4.1}$ structures and from 4 in the tetrahedral [$hM_2M'_2$] holes of the MCo_5D_x and $LaNi_4AlD_{4.1}$ structures to 3 in the $LaNi_5D_{6.0}$ structure (resulting from displacement of the deuterium atoms into the $LaNi_2$ triangular plane).

For the deuterides MCo_5D_x ordered occupation of two of the six [$hM_2M'_2$] holes and two of the three [$hM_2M'_4$] holes in the parent lattice is characteristic. Such an occupation evidently explains the anisotropic expansion of the original hexagonal unit cells leading to their orthorhombic deformation. In accordance with structure models proposed for β-hydrides on the basis of neutron-diffraction data[27], β'- and β''-hydrides have the limiting stoichiometric composition MCo_5H_4, but for β'''-hydrides this composition is MCo_5H_3.

Table 2. Details of crystal structures of hydride phases $M_nM'_mH(D)_x$.

Compound	Space group	Lattice parameters, A			C.n. of hydrogen atoms	Coordination polyhedra of hydrogen atoms*	Shortest interatomic distances, A**			Refs.
		a	*b*	*c*			d_1	d_2	d_3	
β′-$PrCo_6D_{3,6}$	*Cmcm*	8.868	5.431	4.083	6 4	O [$D^{(1)}Pr_2Co_4$] T [$D^{(2)}Pr_2Co_2$]	2.38 (0.55)	1.67 (0.42)	2.45	[27]
β″-$NdCo_5D_{2,8}$	*Im2m*	8.819	5.247	8.093	6 4	O [$D^{(1)}Nd_2Co_4$] T [$D^{(2)}Nd_2Co_2$]	2.37 (0.55)	1.43 (0.18)	2.47	[27]
β‴-$CeCo_5D_{2,55}$	*Cmcm*	8.728	5.105	8.146	6 4	O [$D^{(1)}Ce_2Co_4$] T [$D^{(2)}Ce_2Co_2$]	2.34 (0.52)	1.61 (0.36)	2.30	[27]
$LaNi_5D_{6,0}$	*P321*	5.43	—	4.28	4 3	T [$D^{(1)}LaNi_3$] Tr [$D^{(2)}LaNi_2$]	2.44 (0.56)	1.43 (0.18)	2.29	[132]
$LaNi_5D_{6,0}$	*P31m*	5.410	—	4.293	4 4	T [$D^{(1)}LaNi_3$] T [$D^{(2)}La_2Ni_2$]	2.50 (0.62)	1.45 (0.20)	1.57	[125]
$LaNi_5D_{5,6}$	*P31m*	5.40	—	4.28	4 4	T [$D^{(1)}LaNi_3$] T [$D^{(2)}La_2Ni_2$]	2.50 (0.62)	1.56 (0.31)	1.31	[126]
$LaNi_4AlD_{4,1}$	*P321*	5.300	—	4.242	4 4	T [$D^{(1)}LaNi_2$(Ni, Al)] T [$D^{(2)}La_2$(Ni, Al)$_2$]	2.37 (0.49)	1.48 (0.23)	2.09	[133]
$ZrMoFeD_{2,6}$	*P6$_3$/mmc*	5.420	—	8.826	4 4	T [$D^{(1)}Zr_2$(Mo, Fe)$_2$] T [$D^{(2)}Zr_2$(Mo, Fe)$_2$]	1.86 (0.26)	1.78 (0.38)	1.87	[139]
$ZrMn_2D_{3,0}$	*P6$_3$/mmc*	5.391	—	8.748	4 4 4 4	T [$D^{(1)}Zr_2Mn_2$] T [$D^{(2)}Zr_2Mn_2$] T [$D^{(3)}Zr_2Mn_2$] T [$D^{(4)}Zr_2Mn_2$]	2.05 (0.45)	1.74 (0.48)	***	[140]
$ZrCr_2D_{3,5}$	*Fd3m*	7.697	—	—	4	T [DZr_2Cr_2]	2.06 (0.46)	1.73 (0.45)	2.08	[120]
$ZrCr_2D_{3,1}$	*Fd3m*	7.628	—	—	4	T [DZr_2Cr_2]	2.05 (0.45)	1.75 (0.47)	***	[142]
$CeRu_2D_{5,2}$	*Fd3m*	8.383	—	—	4	T [DCe_2Ru_2]	2.40 (0.58)	1.73 (0.39)	***	[143]
$HfV_2D_{4,0}$****	*I4$_1$/a*	5.42	—	7.85	4	T [DHf_2V_2]	2.01 (0.43)	1.82 (0.47)	2,10	[144]
$ZrV_2D_{3,6}$****	*I4$_1$/a*	5.485	—	7.902	4	T [DZr_2V_2]	2.06 (0.46)	1.80 (0.45)	2,10	[145]
$ZrV_2D_{4,5}$	*Fd3m*	7.913	—	—	4 4	T [$D^{(1)}Zr_2V_2$] T [$D^{(2)}ZrV_3$]	2.04 (0.44)	1.81 (0.46)	***	[146]
$ZrV_2H_{3,7}$	*Fd3m*	7.946	—	—	4 4	T [$H^{(1)}Zr_2V_2$] T [$H^{(2)}ZrV_3$]	1.91 (0.31)	1.85 (0.50)	***	[142]
$ZrV_2D_{2,3}$	*Fd3m*	7.910	—	—	4 4	T [$D^{(1)}Zr_2V_2$] T [$D^{(2)}ZrV_3$]	2.04 (0.44)	1.81 (0.46)	***	[142]
$HfV_2D_{4,0}$*****	*Fd3m*	7.78	—	—	4 4	T [$D^{(1)}Hf_2V_2$] T [$D^{(2)}HfV_3$]	1.98 (0.40)	1.79 (0.44)	2.01	[144]
$ZrTi_2D_4$	*Fd3m*	8.19	—	—	4	T [$DZrTi_3$]	1.92 (0.32)	1.92 (0.46)	2.31	[147]
$HoNi_3D_{1,8}$	*R$\bar{3}$m*	4.991	—	26.12	4 4	T [$D^{(1)}Ho_2Ni_2$] T [$D^{(2)}HoNi_3$]	2.14 (0.37)	1.56 (0.31)	2.13	[148]
α-$TiFeD_{0,057}$	*Pm3m*	2.979	—	—	6 (2)	O [DTi_4Fe_2] (L [DFe_2])	2.11 (0.65)	1.49 (0.22)	2.11	[150]
β-TiFeD	*P222$_1$*	2.966	4.522	4.370	6 6	O [$D^{(1)}Ti_4Fe_2$] O [$D^{(2)}Ti_4Fe_2$]	2.07 (0.61)	1.48 (0.21)	2.29	[97]
$β-TiFeD_{1,1}$	*Pmc2$_1$*	2.956	4.543	4.388	6 6	O [$D^{(1)}Ti_4Fe_2$] O [$D^{(2)}Ti_4Fe_2$]	1.96 (0.50)	1.49 (0.22)	1.96	[96]
$γ-TiFeD_{1,9}$	*P2/m*	4.704	2.380	4.704 γ=97.0°	6 6 6 6	O [$D^{(1)}Ti_4Fe_2$] O [$D^{(2)}Ti_4Fe_2$] O [$D^{(3)}Ti_4Fe_2$] O [$D^{(4)}Ti_2Fe_4$]	1.99 (0.53)	1.71 (0.44)	2.35	[98]
$TiCuD_{0,9}$	*P4/nmm*	3.020	—	6.837	4	T [DTi_4]	1.93 (0.47)	—	2.14	[157]
Th_2AlD_4	*I4/mcm*	7.629	—	6.517	4	T [DTh_4]	2.39 (0.59)	—	1.79	[94]
$LiPtD_{0,66}$	*P31m*	2.728	—	4.226	4 4	T [$D^{(1)}Li_3Pt$] T [$D^{(2)}LiPt_3$]	1.67 (0.11)	1.56 (0.17)	2.73	[160, 161]
$LiPdD_{0,7}$	*P4/mmm*	2.798	—	3.768	6	O [DLi_2Pd_4]	1.88 (0.32)	1.98 (0.60)	2.80	[160]
$Y_6Mn_{23}D_{23}$	*Fm3m*	12.84	—	—	6 4 4 3	O [$D^{(1)}Y_6$] T [$D^{(2)}Y_3Mn$] T [$D^{3}YMn_3$] Tr [$D^{(4)}Y_2Mn$]	2.02 (0.22)	1.68 (0.42)	***	[87]

Table 2 (cont'd).

Compound	Space group	Lattice parameters, A			C.n. of hydrogen atoms	Coordination polyhedra of hydrogen atoms*	Shortest interatomic distances, A**			Refs.
		a	*b*	*c*			d_1	d_2	d_3	
$Th_6Mn_{23}D_{16.2}$	*Fm3m*	12.92	—	—	6 4 5	O [$D^{(1)}Th_6$] T [$D^{(2)}Th_3Mn$] TB [$D^{(3)}Th_2Mn_3$]	2.34 (0.54)	1.68 (0.42)	***	[158]
$ZrNiH_3$	*Cmcm*	3.53	10.48	4.30	3 4	Tr [$H^{(1)}ZrNi_2$] T [$H^{(2)}Zr_3Ni$]	1.93 (0.33)	1.77 (0.52)	2.04	[91]
$ZrCoD_3$	*Cmcm*	3.53	10.48	4.30	5 4	TB [$D^{(1)}Zr_3Co_2$] T [$D^{(2)}Zr_3Co$]	2.13 (0.53)	1.68 (0.43)	2.20	[104]
$LaNiD_{3.7}$	*Cmcm*	3.98	11.94	4.87	5 4 2	TB [$D^{(1)}La_3Ni_2$] T [$D^{(2)}La_3Ni$] L [$D^{(3)}Ni_2$]	2.41 (0.53)	1.56 (0.31)	2.28	[163]
Sr_2RuD_6	*Fm3m*	7.60	—	—	5	TP [DSr_4Ru]	2.69 (0.54)	1.77 (0.43)	2.50	[114]
Mg_2NiD_4*****	*Fm3m*	6.49	—	—	5	TP [DMg_4Ni]	2.30 (0.70)	1.47 (0.22)	2.07	[164]
$ZrVFeD_{3.6}$	$P6_3/mmc$	5.431	—	8.863	4 4 4 4	T [$D^{(1)}Zr_2(V, Fe)_2$] T [$D^{(2)}Zr_2(V, Fe)_2$] T [$D^{(3)}Zr_2(V, Fe)_2$] T [$D^{(4)}Zr(V, Fe)_3$]	2.02 (0.42)	1.70 (0.35)	***	[166]
$ZrVCuD_{4.0}$	$P6_3/mmc$	5.468	—	8.940	4 4 4 4	T [$D^{(1)}Zr_2(V, Cu)_2$] T [$D^{(2)}Zr_2(V, Cu)_2$] T [$D^{(3)}Zr(V, Cu)_3$] T [$D^{(4)}(V, Cu)_4$]	1.81 (0.21)	1.64 (0.20)	***	[166]
$ZrVNbD_{5.4}$	$P6_3/mmc$	5.690	—	9.288	4 4 4 4	T [$D^{(1)}Zr_2(V, Nb)_2$] T [$D^{(2)}Zr_2(V, Nb)_2$] T [$D^{(3)}Zr_2V(V, Nb)$] T [$D^{(4)}ZrV(V, Nb)_2$]	1.93 (0.33)	1.74 (0.27)	***	[166]
$LaNi_{4.5}Al_{0.5}D_{4.5}$	$P6/mmm$	5.431	—	4.236	4 5	T [$D^{(1)}La_2(Ni, Al)_2$] TB [$D^{(2)}La_2Ni_2(Ni, Al)$]	2.49 (0.61)	1.61 (0.18)	***	[170]
$Ti_4Fe_2OD_{2.25}$	*Fm3m*	11.41	—	—	6 4 4	O [$D^{(1)}Ti_6$] T [$D^{(2)}Ti_3Fe$] T [$D^{(3)}Ti_3Fe$]	1.80 (0.34)	1.51 (0.24)	***	[171]
Sr_2IrD_5	*I4/mmm*	5.320	—	7.796	5 5 5	TP [$D^{(1)}Sr_4Ir$] TP [$D^{(2)}Sr_4Ir$] TP [$D^{(3)}Sr_4Ir$]	2.71 (0.56)	1.69 (0.35)	2.39	[174]

*Symbols for polyhedra: O octahedron, T tetrahedron, Tr triangle, TB trigonal bipyramid, TP tetragonal pyramid, L linear.

**$d_1 = d_{M-H}$, $d_2 = d_{M'-H}$, $d_3 = d_{H-H}$. The values in parentheses after d_1 and d_2 are the effective radius of hydrogen, calculated from $r_{H(D)} = d_{M(M')-H(D)} - r_{M(M')}$.

***The shortest H–H distances cannot be determined precisely from the published data because in the structures there are statistically occupied hydrogen atom positions 1.0–2.1 Å apart.

****Low-temperature modification.

*****High-temperature modification.

However, from data on the absorption–desorption isotherm of hydrogen from the same paper[27], with a rise in pressure the composition of the β′- and β‴-hydrides approaches MCo_5H_4 and MCo_5H_3 respectively, but for β‴-hydrides it does not exceed MCo_5H_3, which contradicts the proposed model for the structure [This sentences does not make sense. The Russian probably has a misprint, possibly in the primes (Ed.of Translation)].

In the structures of the β″- and β‴-hydrides the octahedral holes are filled to a lesser degree as compared to the β′-hydride, while for the β‴-deuteride $CeCo_5D_{2.55}$ ordered filling of half of the [hCe_2Co_4] holes occupied in the β′-hydride structure is characteristic[27]. This ordering, and also some deformation of the metal sublattice in the structures of the β″- and β‴-hydrides, leads to doubling of the *c* parameter of their unit cells.

The orthorhombic γ-hydride structure $LaCo_5H_{4.3}$ has not yet been elucidated although a neutron diffraction study has been carried out on it[27].

A number of publications have been devoted to an investigation of the structure of $LaNi_5D_{6+x}$.[40,118,125–128,132,134]. This is partly because the structure of $LaNi_5H(D)_6$ has been studied independently and also simultaneously in the USSR,[118]

Switzerland[125], and Norway[126].† In addition some inaccuracies in the earlier work gave rise to the need for new publications[129,132]. All the structural models proposed for $LaNi_5.D_{6+x}$ differ rather substantially from each other in some of their features, although each of them is quite satisfactorily verified by the specific neutron-diffraction results of the different authors.

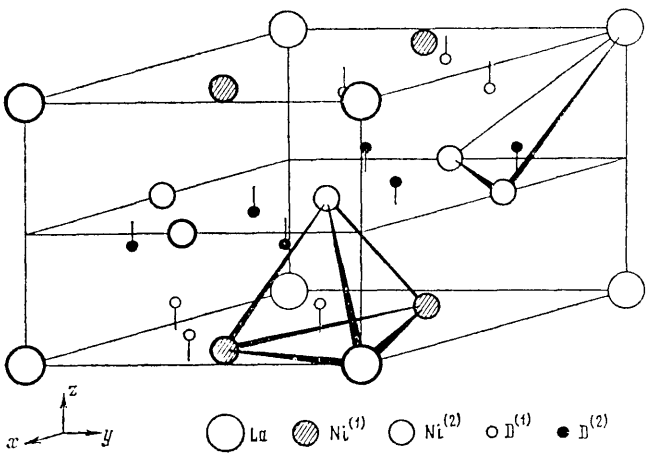


Figure 2. Structure of $LaNi_5D_{6.0}$;[132] the coordination polyhedra of the D atoms are outlined.

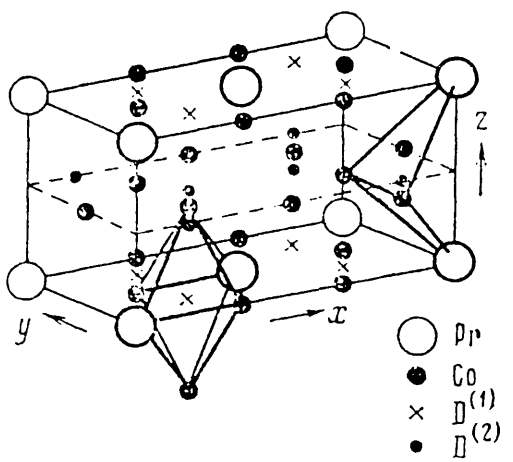


Figure 3. Structure of β'-$PrCo_5D_{3.6}$;[27] the coordination polyhedra of the D atoms are outlined.

†Although the earliest publication on the structure of $LaNiD_{6.8}$ was that of Bowman and co-workers in 1973,[134] their results cannot be considered reliable because of the presence in their structure of D–D and Ni–D interatomic distances equal to 1.30 and 1.17 Å: such small distances are inadmissible from stereochemical considerations; the latter distance is less than the metallic radius of nickel (1.246 Å [16]).

In this situation only those structural results which correlate satisfactorily with the results of research on hydride phases by physicochemical analysis methods can be considered sufficiently conclusive. The broad line n.m.r. method is very informative for crystalline hydrides. The magnitudes of the second moments M_2 determined by this method depend on the H–H and La–H interatomic distances in the hydride phase and indicate clearly the presence of short interatomic contacts. M_2 has been measured experimentally and the values, 12.7 G^2 for $LaNi_5H_{6.0}$ [136] and 13.4 G^2 for $LaNi_{5.3}H_{6.0}$,[135] do not agree with the value M_2 = 20.1 G^2 calculated theoretically by us for the model of the $LaNi_5H(D)_6$ structure proposed by Fischer et al.[125] Hence their hypothesis[125] that positions 6(*d*) in space group *P*31*m* are statistically occupied by deuterium atoms, leading to H–H interatomic distances of 1.58 and 1.68 Å, does not correspond to the facts and the incorrectness of their structural model is indicated.

The same conclusion can be drawn regarding the model proposed[126] for the $LaNi_5D_{5.6}$ structure.

However the model for the $LaNi_5D_{6+x}$ structure proposed[40,132] within the space group *P*321 agrees quite satisfactorily with the experimental n.m.r. results. In considering possible versions of the $LaNi_5H(D)_{6.0}$ structure the assumption was made that in each unit cell the occupation of holes in the metal sublattice by hydrogen atoms proceeds in an ordered way—up to three hydrogen atoms are found in the $[hMM'_3]$ and $[hM_2M'_2]$ holes which are most remote from each other. In this case the minimum H–H interatomic distance is 2.29 Å, which agrees well with the value calculated on the basis of n.m.r. spectra. At the composition $LaNi_5H_{6.0}$ the value calculated for M_2 on this assumption (10.9 G^2) is very close to the experimental values. The n.m.r. results therefore fully confirm the proposed model[40,132] for the $LaNi_5D_{6.0}$ structure.

An argument in favour of this same model is that it is the only model that allows us to explain the presence of the wide homogeneity range in $LaNi_5H_{6+x}$ right up to $LaNi_5H_8$ which exists at −40 °C and a hydrogen pressure of 50 atm,[137] or at room temperature and 1400 atm pressure[32]. In fact the maximum stoichiometric composition which can be achieved by filling all the $[hMM'_3]$ and $[hM_2M'_2]$ holes is $LaNi_5H_9$ whereas in all the other models the composition $LaNi_5H_{6.0}$ cannot be exceeded because of the occurrence of H–H contacts of ~1.5 Å.

The recently published results on the structures of $LaNi_5.D_{6.0}$ and $LaNi_{5-y}M'_yD_x$ (M' = Al, Mn) [127,129] cannot apparently be considered reliable. The authors draw the conclusion that all forms of hole present in the MM'_5 structure including those such as $[hM'_4]$ are statistically occupied by deuterium atoms. However the insertion of hydrogen atoms into holes formed by atoms of elements, which are inactive towards hydrogen and whose binary hydrides are unstable and can be obtained only by the use of special methods, is very improbable. In every case such a conclusion requires careful verification and reliable confirmation by other physicochemical methods as well as structural.

Structural research on hydride phases based on other members of the homologous series of structures MM'_5–MM'_2 has been conducted to a considerably lesser extent than in the case of $MM'_5H(D)_x$. The structure of the hydrides of the Laves phases $MM'_2H(D)_x$ has been studied more completely than the others. The structure of a hydride phase based on an IMC crystallising in the $MgZn_2$ type ($ZrMoFeD_{2.6}$) was first investigated by Yartys' et al.[138,139]. In accordance with the most likely models discussed above for the structure of $MM'_2H(D)_x$ phases, in this deuteride there is ordered insertion of deuterium atoms into two of the four types of $[hZr_2(Mo, Fe)_2]$ holes.

The structure of $ZrMn_2D_{3.0}$ has been investigated (as with ZrMoFe the parent IMC has the $MgZn_2$ type structure).[140] The main results agree with those of Yartys' et al.[138,139]: in $ZrMn_2D_{3.0}$ all four types of $[hZr_2Mn_2]$ hole are statistically occupied.

An attempt to examine the structure of the hydride phase based on $ZrCr_2$, one of whose polymorphic modifications crystallises in the $MgZn_2$ type, was undertaken by Irodova et al.[141] However the authors did not succeed in obtaining a single-phase specimen of the parent IMC and so the structure of the hydride phase was not worked out.

A richer spectrum of structures is obtained by hydrogenating IMC's which crystallise in the $MgCu_2$ type. As in the structures of other Laves phases, there are three different types of hole: $[hM_2M'_2]$, $[hMM'_3]$ and $[hM'_4]$ in the parent $MgCu_2$ structure. For the structures $ZrCr_2D_{3.5}$,[120] $ZrCr_2D_x$ (x = 2.9, 3.1, 3.8),[142] $TiCr_2D_{0.15}$,[49]# $CeRu_2D_{5.2}$,[143] and the low-temperature modifications $HfV_2D_{4.0}$ [144] and $ZrV_2D_{3.6}$,[145] filling of only the largest-in-volume $[hM_2M'_2]$ holes, when their periphery includes the greatest number of atoms of element M (Zr, Ti, Ce, Hf), is characteristic as in hydrides based on IMC's with the $MgZn_2$ type structure. Besides these, two other structural variations are known—a mixed filling of the $[hM_2M'_2]$ and $[hMM'_3]$ holes in the high-temperature modifications of the hydride phases based on HfV_2 and ZrV_2 (the $ZrV_2D_{4.5}$,[146] $ZrV_2H_{3.7}$,[142] $ZrV_2D_{2.3}$,[142] and $HfV_2.D_{4.0}$ [144] structures) and filling of only the $[hMM'_3]$ holes ($ZrTi_2D_4$ structure[147]), as a result of which a spinel type structure is formed§.

It is of interest that in structures with mixed filling of $[hM_2M'_2]$ and $[hMM'_3]$ holes, the degree of filling is identical for zirconium and hafnium compounds. In contrast to $ZrV_2.H(D)_x$ phases in which hydrogen atoms are found in approximately equal or similar quantities in the two types of hole, in the $HfV_2D_{4.0}$ structure five times as many atoms occur in the $[hM_2M'_2]$ holes as in the $[hMM'_3]$ holes. The phase transition which occurs at 298 K in $HfV_2D_{4.0}$ is accompanied by a reduction in the lattice symmetry from f.c.c. to body-centred tetragonal (b.c.t.) and by a redistribution of deuterium atoms in the holes in the metal matrix; the $[hMM'_3]$ holes remain vacant but the $[hM_2M'_2]$ holes are filled in an ordered manner—of the three possible positions which are related by symmetry operations in the f.c.c. unit cell but are independent in the b.c.t. cell, only one is occupied. Similar results were obtained for $ZrV_2D_{3.6}$.[145]

Neutron-diffraction studies of hydride phases based on IMC's located in the homologous series of related compounds between the compositions MM'_5 and MM'_2 have been carried out for only one compound, namely the deuteride $HoNi_3D_{1.8}$ based on an IMC with the $PuNi_3$ type structure[40,148]. As was expected, the structure of $HoNi_3D_{1.8}$ corresponds to one of the most probable models for the structure—a large proportion of the deuterium atoms occupy the $[hHo_2Ni_2]$ holes, which are the most preferred from the point of view of their size and periphery, and which are similar to the holes with the same periphery and which are occupied in the MM'_5D_x deuteride structures, and they are located near the boundary of the $CaCu_5$ and $MgZn_2$ type portions of the structure (Fig.4). However, the most distinctive feature of the $HoNi_3D_{1.8}$ structure is the occupation of holes with an $HoNi_3$ periphery. This type of hole lies within the $MgZn_2$ type section of the structure and is vacant in the $ZrMoFeD_{2.6}$ and $ZrMn_2D_{3.0}$ structures.

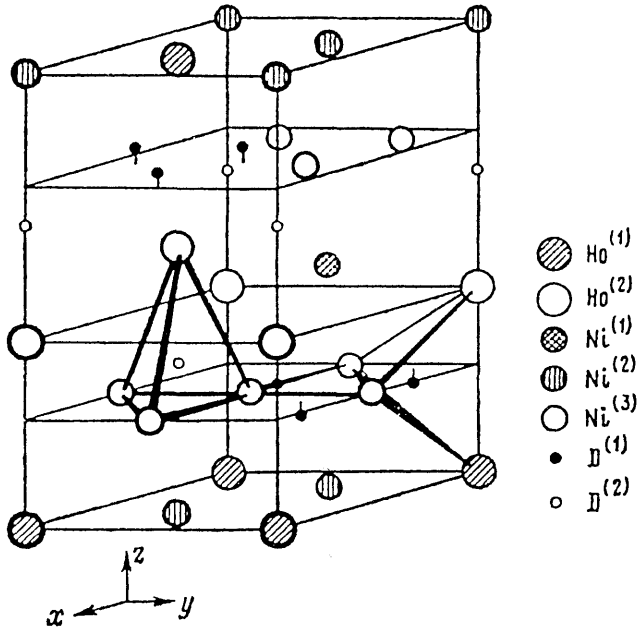


Figure 4. Structure of $HoNi_3D_{1.8}$ [148] (z = 0–1/3); the coordination polyhedra of the D atoms are outlined.

The special features of the structure of $HoNi_3D_{1.8}$ permit the unusual type of deformation of the metal matrix on the insertion of hydrogen into it (expansion of the unit cell only in the z axis direction) to be explained. Analysis of the M–M interatomic distances in the $HoNi_3$ structure shows that they vary over a fairly considerable range—some of them exceed the sum of the corresponding metal radii while other distances are markedly "shortened", i.e. significantly less than the sum of the radii, with all the "shortened" distances lying either in planes perpendicular to the z axis of the unit cell, or at a very small angle to these planes, and the "elongated" distances, on the other hand, lying either parallel to the z axis or at some angle to this axis. It thus seems quite natural to suppose that expansion of the unit cell must take place most easily in that direction where resistance to the deformation resulting from the insertion of hydrogen atoms is least. It is evidently just this ease of deformation of the "elongated" M–M bonds, which lie along the z axis, that explains the expansion of the unit cell only in the [001] direction. The holes in the metal matrix preferred for insertion of hydrogen atoms are of course those whose periphery contains "elongated" M–M bonds. As might have been supposed two of just such holes are occupied in the $HoNi_3D_{1.8}$ structure.

#The stoichiometric composition corresponds to the α-solution.

§Although $ZrTi_2D_4$ is formed by the reaction of deuterium with an alloy of composition $ZrTi_2$ which does not possess the $MgCu_2$ type structure, in the structure of this deuteride the metal atoms occupy crystallographic positions characteristic of a C15 type phase and therefore the $ZrTi_2D_4$ structure can be regarded as a derivative of insertion type in the structure of the hypothetical compound "$ZrTi_2$".

The choice of hydride phases based on other structural types of IMC which have been investigated by neutron diffraction has been to a considerable degree accidental. Much interest has been shown for some time past in the study of the structure of hydride phases formed on the basis of TiFe. This is quite understandable as $TiFeH_{1.9}$ is one of the most promising substances for hydrogen storage[149]. There have been neutron-diffraction studies of all the hydride phases formed in the TiFe–$H(D)_2$ system: α, β, and γ with compositions corresponding to the formulae $TiFeD_{0.057}$,[150] $TiFeD_{1.0-1.1}$,[96,97] and $TiFeD_{1.9}$.[98]

These researches showed that deuteriation is not in this case accompanied by reorganisation of the parent metal matrix and leads only to some deformation. In the α-phase $TiFeD_{0.057}$ [150] there is ordered occupation by the deuterium atoms of one of the three octahedral holes with a Ti_4Fe_2 periphery present in the unit cell of TiFe. The difference between the Fe–D interatomic distances and the metallic radius of iron (0.22 Å) is significantly less than the corresponding value for the Ti–D distances (0.65 Å). The coordination of the deuterium atom can be interpreted as linear $[DFe_2]$ and its coordination number is as a result decreased from 6 to 2.

Further introduction of hydrogen into the structure gives the β-phase which has a composition close to $TiFeH(D)_{1.0}$.[96,97] The orthorhombic $TiFeD_{1.1}$ structure was examined for the first time by neutron diffraction by Thompson et al.[96], who showed that the deuterium atom $D^{(1)}$ occupies the octahedral $[hTi_4Fe_2]$ hole. The small amount of deuterium in excess of the composition $TiFeD_{1.0}$ occurs in octahedral holes of a second type, also having a Ti_4Fe_2 periphery, but they are somewhat displaced from the ideal centres. A second examination of this structure[97] confirmed the main results of Thompson et al.[96], but found that the $D^{(2)}$ atoms are exactly in the centres of the $[hTi_4Fe_2]$ holes.

In the *P–C* diagram of the TiFe–H_2 system[151] two two-phase regions α + β and β + γ exist. However, on the basis of unverified data[152] as to the existence of a subsidiary plateau in the composition range $1 < x < 1.4$ on the isotherm for absorption–desorption of hydrogen by the hydride phase $TiFeH_x$ at 274 K (note that these data were not confirmed in a study of deuterated specimens[153]), Schefer et al.[153] concluded that there is a hydride phase close in composition to $Ti_3Fe_3D_4$. Examination of the structure of this phase showed that it is isostructural with $TiFeD_{\sim 1}$ and further introduction of deuterium atoms into it takes place in the holes filled with the $D^{(2)}$ atoms in the $TiFeD_{\sim 1}$ structure.

The γ-phase $TiFeD_{1.9}$ (Fig. 5) has a monoclinic unit cell in which the deuterium atoms occupy four different positions[98]. Three of these are octahedral holes with a Ti_4Fe_2 periphery, two out of the three corresponding to the positions of atoms $D^{(1)}$ in the β-phase structure, but for atom $D^{(4)}$ the coordination polyhedron is the octahedron $[D^{(4)}Ti_2Fe_4]$. Rather unexpectedly the holes occupied by atoms $D^{(2)}$ in the β-phase structure are vacant in the γ-phase.

The TiFe–$H(D)_2$ system was also studied with neutron diffraction by West German authors[154,155]. The results obtained are on the whole in agreement with the data discussed above[96,97].

A detailed discussion of all the neutron-diffraction data on the TiFe–$H(D)_2$ system has been given in a recent review[156].

$TiCuD_{0.9}$, which has been examined by neutron diffraction[157], was obtained by starting with the γ-modification of the IMC which possesses tetragonal symmetry. Unfortunately the reliability of the experimental results is reduced considerably by the presence as an impurity in the IMC of another of its allotropes, the δ-phase, which also has a tetragonal structure and whose reaction with hydrogen was not studied by these authors. In this connection the exclusion of some parts of the neutron-diffraction pattern (in which the diffraction lines of the γ- and δ-hydrides $TiCuD_x$ were superposed) from consideration was not sufficiently justified. Nevertheless these results are quite reasonable and correspond to the most probable model for the deuteride structure: the holes occupied by hydrogen are those most preferred for filling, the tetrahedral holes $[hTi_4]$ which have a periphery of atoms of the element (titanium) more active with respect to hydrogen.

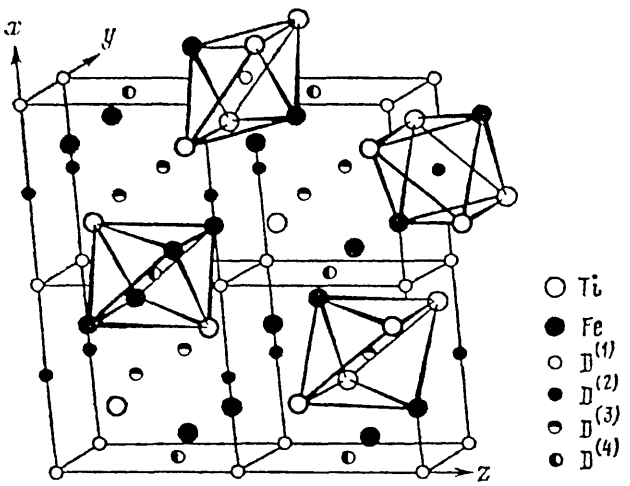


Figure 5. Structure of γ-$TiFeD_{1.9}$; the coordination polyhedra of the D atoms are outlined.

The investigation of the deuterides $Y_6Mn_{23}D_x$ (x = 8.3, 18.0, 23.0) based on an IMC with the Th_6Mn_{23} type structure[87] is of considerable interest. The parent IMC crystallises with a complex cubic structure, the unit cell of which contains 116 metal atoms and has 9 different positions which can be occupied by deuterium atoms. The sequence of filling of the different positions as the deuterium content is increased corresponds on the whole to the rules set out above for the structure of multicomponent IMC hydrides. When the first hydride phase $Y_6Mn_{23}D_{8.3}$ is formed, the deuterium atoms enter the $[hY_6]$ and $[hY_3Mn]$ holes whose periphery contains the largest contribution of atoms of yttrium which is the element active towards hydrogen. In the second phase $Y_6Mn_{23}D_{18}$ the $[hYMn_3]$ holes are filled as well and then in the $Y_6Mn_{23}.D_{22.9}$ structure deuterium atoms enter the $[DY_2Mn]$ position with trigonal planar coordination. As expected, the $[hMn_4]$ holes formed by manganese, which is the inactive element with respect to hydrogen, are not filled in any of the deuterides. From the last of the proposed models we may arrive at the maximum stoichiometric composition for the hydride phase of $M_6M'_{23}H_{33}$.

$Th_6Mn_{23}D_{16.2}$ has been examined by neutron diffraction[158]. The structure of this compound might be expected to be analogous to that of $Y_6Mn_{23}D_{18}$ described above. It was however found that they are not isostructural—firstly, the deuterium atoms are displaced substantially from the centres of the $[hMM'_3]$ holes and two holes of this type are arranged with an Mn_3 triangular face in common, leading to a change in the form of the coordination polyhedron of the deuterium

atom from a tetrahedron in $Y_6Mn_{23}D_{18}$ to a trigonal bipyramid $[D^{(3)}Th_2Mn_3]$. In addition, the degree of occupation of the $[hM_6]$ holes in the structure of the Th compound is relatively small, in contrast to the $Y_6Mn_{23}D_{18}$ structure in which they are completely filled[87].

The intermetallic compound LiPt crystallises in the LiRh type structure[159], which is a superstructure to the Mg type. In the $LiPtD_{0.66}$ structure[160,161] the deuterium atoms occupy the tetrahedral holes in the hexagonal close packing. The coordination polyhedra of the deuterium atoms are the $[D^{(1)}.Li_3Pt]$ and $[D^{(2)}LiPt_3]$ tetrahedra. The $LiPtD_{0.66}$ structure has no analogues among the structures of binary hydrides with hexagonal close-packed metal atoms, for which as is known filling of octahedral, and not tetrahedral, holes is typical.

The intermetallic compound LiPd exists in two polymorphic modifications, with structures of the LiRh and CsCl types[162]. Only one of these (the LiRh type) is capable of reacting with hydrogen, and the hydride formed has a tetragonal structure[160]. The hydrogenation process is accompanied by reorganisation of the metal matrix from the LiRh type to a tetragonally distorted CsCl type. If the $LiPdD_{0.7}$ structure[160] is regarded as derived by insertion to the CsCl type, then the deuterium atoms are found to occupy only one out of three octahedral holes present in the b.c.c. unit cell with Li_2Pd_4 periphery, evidently as a result of which there is an anisotropic expansion of the structure.

The structure of Th_2AlD_4 [94] can be regarded as a packing of $[AlTh_8]$ tetragonal antiprisms with aluminium at the centre and unfilled $[hTh_4]$ tetrahedra, which the hydrogen atoms occupy on introduction into the IMC lattice. At the stoichiometric composition Th_2AlD_4 all 16 of these tetrahedra are occupied but when D/Th_2Al is less than 4 the filling is disordered.

The $ZrNiH_3$ structure[91] is a derivative of the insertion type to the CrB type structure. The structure of ZrNi consists of layers of $[NiZr_6]$ trigonal prisms with nickel at the centre and layers of unoccupied rhombic pyramids and tetrahedra of zirconium atoms alternating one above the other[25]. In the $ZrNiH_3$ structure the hydrogen atoms of one sort are at the centre of the base of the trigonal prisms; their coordination polyhedron is the trigonal bipyramid $[H^{(1)}Zr_3Ni_2]$. The hydrogen atom is displaced from the ideal position at the centre of the bipyramid in the plane passing through the nickel atoms and one of the zirconium atoms. The coordination of the atom $H^{(1)}$ can be regarded as triangular $[H^{(1)}ZrNi_2]$. The hydrogen atoms of the second sort occupy distorted tetrahedra $[H^{(2)}Zr_3Ni]$.

Deuteriation of the intermetallic compound ZrCo, which possesses the CsCl type structure, gives $ZrCoD_3$, isostructural with $ZrNiH_3$, with ordered Zr and Co atoms in the CrB type[104]. In contrast to the $ZrNiH_3$ structure, the atom $D^{(1)}$ is only slightly displaced from the centre of the trigonal bipyramid, so that it has a c.n. of 5, $[D^{(1)}Zr_3Co_2]$. Atom $D^{(2)}$, as in the $ZrNiH_3$ structure, has a c.n. of 4 and tetrahedral coordination $[D^{(2)}Zr_3Co]$.

The third representative of hydride phases based on an IMC with the CrB type structure, whose structure is known, is $LaNiD_{3.7}$. When the D/LaNi ratio exceeds 3.0, the deuterium atoms have linear coordination, which is unusual for metal hydrides, with nickel atoms as neighbours (Fig.6).[124,163] The structure of $LaNiD_{3.7}$, together with $TiFeD_{0.057}$,[150] is a rare example of a metal hydride structure in which the hydrogen atoms have a c.n. of 2. The atoms $D^{(1)}$ and $D^{(2)}$ in this structure occupy the same positions as in the structures of Zr-containing compounds with trigonal bipyramids and tetrahedra as coordination polyhedra.

Sr_2IrD_5 and Sr_2RuD_6 [114] are obtained by deuteriation of a mixture of SrD_2 and Ir (or Ru). Their structures are cubic with the metal atoms ordered in the antifluorite positions. The $Sr_2M'D_{6-x}$ structure (M' = Ir, Ru) can be regarded as a packing of equal numbers of vacant and occupied cubes $[hSr_8]$ and $[M'Sr_8]$. The deuterium atoms are centred over all the cube faces, and their coordination polyhedron is a tetragonal pyramid $[DSr_4M']$. In defect structures ($H/Sr_2M' < 6$) the hydrogen atoms are statistically distributed in the holes. These hydrides are isostructural with K_2PtCl_6.

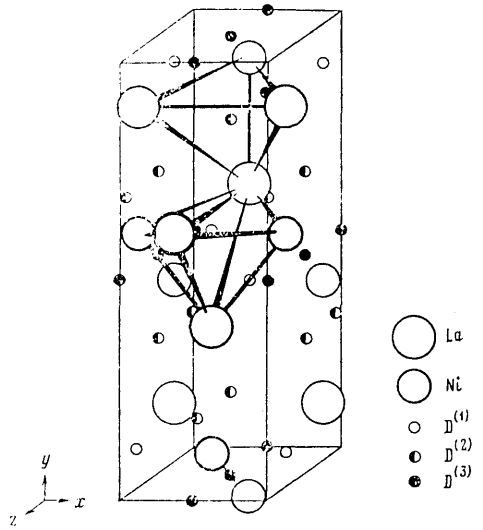


Figure 6. Structure of $LaNiD_{3.7}$; the coordination polyhedra of the D atoms are outlined.

Among compounds crystallising in the K_2PtCl_6 type the greatest defect nature of the hydrogen sublattice is shown by the high-temperature modification of Mg_2NiD_4 [164] (the phase transition is at 483–518 K) which, in contrast to the phases discussed above, can be obtained by starting with Mg_2Ni. In the deuteration process the hexagonal Mg_2Ni structure reorganises to the cubic antifluorite type. However, the defect nature of the sublattice does not lead to a change in the c.n. of the deuterium, which is 5, nor in its coordination ($[DMg_4.Ni]$ tetragonal pyramid).

The details of the crystal structures of the hydride phases described above are given in Table 2, and the crystallographic data for the parent IMC's and hydride phases based on them are in Table 3.

Table 2 shows the shortest M–H and H–H interatomic distances as well as the symmetry of the structures and the form of the coordination polyhedron of the deuterium atoms. In the majority of the structures the mean values of the M–H(D) distances are equal to the sum: r_M + 0.4 to r_M + 0.6 Å. They are as a rule similar in size to the analogous distances in the structures of binary hydrides.

However, for half of the structures in Table 2 (to be precise, 17 out of 35) the minimum effective radius of the hydrogen atom is substantially less, lying in the ranges 0.18 to 0.26 Å (10 structures) or 0.27–0.33 Å (7 structures), and a comparable value occurs for only two binary hydrides (0.31 to 0.32 Å in Y and Sc trihydrates[18,14]).

Table 3. Crystallographic data for hydride phases $M_xM'_yH_z$ and the parent intermetallic compounds.

IMC	Structure type	Lattice parameters, A			$H/M_xM'_y$	Lattice parameters, A			$\Delta L/V_a$, %	ΔV/atoms of H, A^3	Refs.
		a	*b*	*c*		*a*	*b*	*c*			
LiSr	*	—	—	—	3.0	3.833	—	—	—	—	[110]
Li_4Rh	*	—	—	—	4.0	6.338	—	4.113	—	—	[116]
Li_5Rh	*	—	—	—	5.0	3.380	9.020	8.895	—	—	[116]
LiBa	*	—	—	—	3.0	4.023	—	—	—	—	[110]
LiEu	*	—	—	—	3.0	3.796	—	—	—	—	[110]
Mg_2Ni **	Mg_2Ni	5.19	—	13.22	4.0	6.497	6.414	6.601	33.6	4.3	[102]
Mg_2Ni	Mg_2Ni	5.19	—	13.22	4.0	6.490	—	—	33.0	4.2	[102]
$CaNi_2$	$MgCu_2$	7.251	—	—	3.4	7.7	—	—	19.8	2.8	[55]
$CaNi_3$	$PuNi_3$	5.030	—	24.27	4.6	5.444	—	26.56	28.2	3.6	[55]
$CaNi_5$	$CaCu_5$	4.950	—	3.936	4.5	5.305	—	4.009	17.0	3.2	[55]
$CaNi_5$	$CaCu_5$	4.950	—	3.936	5.0	5.250	9.194	8.042	16.2	2.7	[177]
Ca_2Ru	*	—	—	—	6.0	7.24	—	—	—	—	[114]
Ca_2Rh	*	—	—	—	5.0	7.24	—	—	—	—	[114]
Ca_2Pd_2	*	—	—	—	4.0	5.22	—	—	—	—	[111]
Ca_2Ir	*	—	—	—	5.0	7.29	—	—	—	—	[114]
$CaNi_4B$	$CeCo_4B$	5.066	—	6.846	3.5	5.256	—	7.021	10.4	2.3	[55]
$ScMn_2$	$MgZn_2$	5.033	—	8.278	3.8	5.49	—	8.96	28.8	3.4	[45]
$ScFe_{1.96}$	$MgZn_2$	4.965	—	8.125	2.0	5.279	—	8.507	18.4	4.0	[187]
$ScFe_2$	$MgNi_2$	4.972	—	16.28	2.7	5.255	—	17.04	16.9	2.7	[44]
$ScCo_2$	$MgCu_2$	6.922	—	—	2.8	7.334	—	—	18.9	2.8	[44]
$ScNi_2$	$MgCu_2$	6.934	—	—	1.6	7.141	—	—	21.2	2.4	[44]
Ti_3Al	Mg_3Cd	5.793	—	4.655	1.4	3.28	—	—	10.6	1.3	[105]
Ti_3Al	Mg_3Cd	5.793	—	4.655	6.4	4.35	—	—	6.4	0.8	[105]
$TiCr_{1.8}$	$MgCu_2$	6.94	—	—	3.4	7.30	5.18	4.94	11.6	1.5	[49]
$TiCr_{1.9}$	$MgZn_2$	4.927	—	7.961	2.9	5.171	—	8.518	17.4	5.2	[48]
TiFe	CsCl	2.975	—	—	1.0***	2.966	4.522	4.369	11.4	3.0	[97]
TiFe	CsCl	2.975	—	—	1.1***	2.956	4.543	4.388	12.0	3.1	[96]
TiFe ***	CsCl	2.975	—	—	1.9***	4.704	2.839	4.704	18.2	2.5	[98]
TiCo	CsCl	2.994	—	—	1.0	6.44	—	9.06	6.2	1.7	[106]
TiNi	CsCl	3.013	—	—	1.0	24.8	—	—	8.7	2.4	[78]
Ti_2Ni	Ti_2Ni	11.32	—	—	0.5	11.50	—	—	4.8	4.4	[78]
Ti_2Ni	Ti_2Ni	11.32	—	—	1.0	11.60	—	—	7.6	3.4	[78]
Ti_2Ni	Ti_2Ni	11.32	—	—	2.0	11.80	—	—	13.3	3.0	[78]
Ti_2Ni	Ti_2Ni	11.32	—	—	2.5	11.90	—	—	16.2	2.9	[78]
TiCu	TiCu	3.108	—	5.887	0.9***	3.02	—	6.837	9.0	2.8	[157]
Ti_2Pd	$MoSi_2$	3.090	—	10.054	2.0	2.96	3.16	11.39	10.9	2.6	[100]
V_3Ga	Cr_3Si	4.818	—	—	2.0	4.859	—	—	9.1	2.5	[101]
Sr_2Pd	*	—	—	—	1.0	7.97	—	—	—	—	[110]
Sr_2Pd	*	—	—	—	4.0	9.96	—	—	—	—	[111]
Sr_2Ir	*	—	—	—	5.0	7.62	—	—	—	—	[114]
YMn_2	$MgCu_2$	7.680	—	—	2.9	8.163	—	—	20.1	3.9	[57]
YMn_2	$MgCu_2$	7.680	—	—	2.9	8.274	—	—	25.0	4.9	[57]
YMn_2	$MgCu_2$	7.680	—	—	*****	8.27	—	—	24.9	—	[60]
Y_6Mn_{23}	Th_6Mn_{23}	12.44	—	—	25	12.84	—	—	10.0	1.9	[57]
YFe_2	$MgCu_2$	7.348	—	—	2.0	7.679	—	—	14.1	3.5	[185]
YFe_2	$MgCu_2$	7.348	—	—	3.6	16.07	—	—	30.8	4.2	[185]
YFe_2	$MgCu_2$	7.356	—	—	4.2	7.84	—	—	21.1	2.5	[56]
YFe_3	$PuNi_3$	5.137	—	24.61	4.8	5.375	—	26.46	17.9	2.3	[56]
Y_6Fe_{23}	Th_6Mn_{23}	12.12	—	—	21.5	12.47	—	—	8.3	1.7	[56]
YCo_2	$MgCu_2$	7.214	—	—	3.6	15.54	—	—	12.5	3.2	[61]
YCo_3	$PuNi_3$	5.013	—	24.35	1.0	5.013	—	25.86	6.2	3.7	[56]
YCo_3	$PuNi_3$	5.013	—	24.35	2.0	5.000	—	26.23	7.2	2.1	[70]
YCo_3	$PuNi_3$	5.013	—	24.35	3.7	5.268	—	26.46	20.0	3.2	[70]
Y_2Co_7	Gd_2Co_7	5.002	—	36.15	1.5	4.988	—	37.72	3.8	3.3	[72]
Y_2Co_7	Gd_2Co_7	5.002	—	36.15	3.0	5.138	—	38.45	11.6	5.0	[72]
YNi_2	$MgCu_2$	7.154	—	—	3.0	7.569	—	—	18.4	2.6	[185]
YNi_2	$MgCu_2$	7.184	—	—	3.6	7.563	—	—	17.7	2.3	[56]
YNi_3	$PuNi_3$	4.973	—	24.42	1.2	4.996	—	24.35	0.6	0.3	[56]
YNi_3	$PuNi_3$	4.977	—	24.44	1.6	4.987	—	26.82	13.2	4.6	[188]
YNi_3	$PuNi_3$	4.973	—	24.37	4.0	5.267	—	26.57	22.3	3.2	[73]
YNi_3	$PuNi_3$	4.977	—	24.44	4.2	5.283	—	26.82	25.0	3.4	[190]
YNi_4Mn	UNi$_5$	6.972	—	—	4.5	7.3	—	—	7.4	2.8	[95]
Zr_4Al_3	Zr_4Al_3	5.433	—	5.390	3.6	5.484	—	5.595	5.7	2.2	[99]
ZrV_2	$MgCu_2$	7.416	—	—	4.8	7.956	—	—	23.5	2.5	[39]
$ZrCr_2$	$MgZn_2$	5.106	—	8.273	2.7***	5.367	—	8.754	16.9	2.9	[40]
$ZrCr_2$	$MgCu_2$	7.207	—	—	3.5***	7.697	—	—	21.9	2.9	[120]
$ZrMn_{1.8}$	$MgZn_2$	5.045	—	8.284	2.0	5.495	—	8.889	27.2	6.2	[174]
$ZrMn_{2.2}$	$MgZn_2$	4.988	—	8.200	4.0	5.424	—	8.682	25.2	2.8	[47]
$ZrFe_2$	$MgCu_2$	7.046	—	—	0.2	7.060	—	—	1.9	3.2	[38]
ZrCo	CsCl	3.196	—	—	3.0***	3.53	10.48	4.30	22.0	2.4	[104]
ZrNi	CrB	3.258	9.941	4.094	1.0	3.28	10.04	4.24	5.3	1.7	[90]
ZrNi	CrB	3.258	9.941	4.094	3.0	3.53	10.48	4.30	20.0	2.2	[91]
$ZrMo_2$	$MgCu_2$	7.548	—	—	1.4	7.698	—	—	6.8	2.6	[38]
Zr_2Pd	$MoSi_2$	3.297	—	10.92	2.7	3.41	—	11.42	11.9	2.6	[100]
ZrAg	ZrAg	3.348	—	6.603	1.0	3.53	—	7.35	12.2	4.4	[92]
ZrTiNi	$MgZn_2$	5.147	—	8.320	3.7	5.490	—	8.909	21.7	2.2	[38]
ZrVAl	$MgZn_2$	5.297	—	8.634	2.1	5.426	—	8.869	8.1	2.0	[39]
ZrVCr	$MgCu_2$	7.281	—	—	*****	7.759	—	—	21.0	—	[64]
ZrVFe	$MgZn_2$	5.050	—	8.488	4.0	5.406	—	8.922	23.2	2.7	[39]
ZrVCo	$MgZn_2$	5.053	—	8.232	4.0	5.508	—	8.839	23.5	2.7	[39]
ZrVNi	$MgZn_2$	5.013	—	8.196	2.8	5.391	—	8.802	24.2	3.8	[39]
ZrVNi	$MgCu_2$	7.112	—	—	3.7	7.542	—	—	19.3	2.3	[39]
ZrVCu	$MgZn_2$	5.154	—	8.384	4.0	5.473	—	8.934	20.2	2.4	[39]
ZrVNb	$MgZn_2$	5.348	—	8.624	5.4	5.719	—	9.255	23.3	2.4	[39]
ZrMoCr	$MgZn_2$	5.204	—	8.523	2.4	5.415	—	8.974	12.0	2.1	[39]
ZrMoFe	$MgZn_2$	5.172	—	8.463	2.6***	5.520	—	8.826	14.5	2.7	[167]
$LaCo_2$	$MgCu_2$	7.239	—	—	3.8	5.592	5.488	7.88	26.8	3.3	[64]
$LaCo_5$	$CaCu_5$	5.109	—	3.970	3.4	8.973	5.413	4.088	11.1	2.8	[27]
$LaCo_5$	$CaCu_5$	5.109	—	3.970	4.2	9.495	5.381	3.966	11.3	2.8	[27]
LaNi	CrB	3.81	10.53	4.37	3.7***	3.982	11.94	4.873	32.2	3.8	[124]
$LaNi_5$	$CaCu_5$	5.015	—	3.987	6.0	5.426	—	4.269	18.9	2.9	[40]
$LaRu_2$	$MgCu_2$	7.702	—	—	4.0	8.42	—	—	30.7	4.4	[53]
$LaNi_4Al$	$CaCu_5$	5.066	—	4.070	4.3	5.319	—	4.225	11.5	3.1	[29]
$LaNi_4Al$	$CaCu_5$	5.066	—	4.069	4.1***	5.300	—	4.242	14.1	3.1	[133]
$CeCo_3$	$PuNi_3$	4.955	—	24.75	4.0	4.956	—	32.69	32.1	4.7	[56]
Ce_2Co_7	Ce_2Ni_7	4.930	—	24.46	6.0	4.949	—	29.69	21.8	4.7	[56]
Ce_2Co_7	Ce_2Ni_7	4.497	—	24.50	5.3	5.007	—	24.99	4.5	1.1	[42]
$CeCo_5$	$CaCu_5$	4.922	—	4.049	2.5	8.726	5.105	8.146	7.6	2.5	[27]
$CeNi_2$	$CeNi_2$	4.960	—	16.55	3.0	4.920	—	21.64	28.7	5.6	[56]
Ce_2Ni_7	Ce_2Ni_7	4.927	—	24.45	4.0	4.920	—	29.63	20.8	6.7	[56]
$CeRu_2$	$MgCu_2$	7.546	—	—	5.2***	8.383	—	—	37.1	3.8	[143]
$CeNi_4Al$	$CaCu_5$	4.943	—	4.085	3.7	5.227	—	4.186	11.5	3.4	[29]
$PrCo_2$	$MgCu_2$	7.306	—	—	4.0	15.86	—	—	28.2	3.4	[61]
$PrCo_3$	$PuNi_3$	5.068	—	24.79	1.8	5.091	—	27.57	12.2	4.2	[40]
$PrCo_4$	$PuNi_3$	5.068	—	24.79	3.7	5.380	—	27.30	24.1	3.9	[40]
Pr_2Co_7	Ce_2Ni_7	5.058	—	24.51	2.5	5.081	—	26.30	8.3	4.5	[72]
Pr_2Co_7	Ce_2Ni_7	5.058	—	24.51	5.8	5.312	—	26.04	17.1	4.0	[72]
$PrCo_5$	$CaCu_5$	5.022	—	3.989	2.8	8.837	5.261	8.110	8.1	2.5	[27]
$PrCo_5$	$CaCu_5$	5.022	—	3.989	3.6	8.868	5.341	4.083	11.1	2.7	[27]
$PrNi_4Al$	$CaCu_5$	5.023	—	4.064	3.7	5.254	—	4.203	11.3	3.2	[29]
$NdMn_{23}$	Th_6Mn_{23}	12.67	—	—	*****	13.24	—	—	14.1	—	[192]
$NdCo_2$	$MgCu_2$	7.294	—	—	3.8	7.95	—	—	29.5	3.8	[61]
$NdCo_3$	$PuNi_3$	5.055	—	24.70	1.8	5.055	—	27.40	10.9	3.7	[70]
$NdCo_3$	$PuNi_3$	5.055	—	24.70	4.0	5.357	—	27.24	23.9	3.6	[70]
Nd_2Co_7	Ce_2Ni_7	5.053	—	24.43	2.7	5.069	—	26.29	8.3	4.1	[72]
Nd_2Co_7	Ce_2Ni_7	5.053	—	24.43	6.2	5.268	—	25.92	15.3	3.3	[72]
$NdCo_5$	$CaCu_5$	5.020	—	3.977	2.7	8.819	5.247	8.092	8.1	2.5	[27]
$NdRu_2$	$MgZn_2$	5.323	—	9.004	5.5	5.88	—	9.62	30.3	3.0	[146]
$NdNi_4Al$	$CaCu_5$	5.004	—	4.067	4.0	5.229	—	4.183	11.2	2.7	[29]
$SmMn_2$	$MgZn_2$	5.111	—	8.976	3.8	5.49	—	8.86	13.9	1.9	[68]
Sm_6Mn_{23}	Th_6Mn_{23}	12.57	—	—	*****	13.04	—	—	11.6	2.4	[68]
Sm_6Mn_{23}	Th_6Mn_{23}	12.56	—	—	*****	13.13	—	—	14.2	—	[192]
$SmFe_2$	$MgCu_2$	7.417	—	—	*****	8.00	—	—	29.7	—	[52]
$SmFe_3$	$PuNi_3$	5.187	—	24.91	4.2	5.40	—	27.09	17.9	2.7	[68]
$SmCo_3$	$CaCu_5$	4.995	—	3.965	2.5	8.752	5.224	8.056	7.4	2.6	[27]
$SmRu_2$	$MgZn_2$	5.298	—	8.939	4.6	5.84	—	9.53	29.5	3.5	[146]
$SmNi_4Al$	$CaCu_5$	4.980	—	4.050	3.6	5.193	—	4.155	11.1	2.8	[29]
Eu_2Ru	*	—	—	—	6.0	7.566	—	—	—	—	[115]
Eu_2Ir	*	—	—	—	5.0	7.580	—	—	—	—	[112]
$GdMn_2$	$MgCu_2$	7.724	—	—	*****	8.051	—	—	8.7	—	[42]
Gd_6Mn_{23}	Th_6Mn_{23}	12.51	—	—	*****	12.95	—	—	10.9	—	[42]
$GdFe_2$	$MgCu_2$	7.389	—	—	3.6	16.06	—	—	28.8	3.8	[185]
$GdFe_3$	$PuNi_3$	5.167	—	24.71	3.1	5.387	—	27.01	17.5	3.8	[71]
$GdCo_2$	$MgCu_2$	7.262	—	—	3.9	5.532	5.437	7.89	23.9	2.9	[61]
$GdCo_3$	$PuNi_3$	5.037	—	24.51	2.0	5.021	—	27.34	10.8	3.2	[70]
$GdCo_3$	$PuNi_3$	5.037	—	24.51	3.7	5.291	—	26.88	21.0	3.4	[70]
Gd_2Co_7	Gd_2Co_7	5.017	—	36.31	2.6	5.042	—	39.04	7.3	3.7	[72]
Gd_2Co_7	Gd_2Co_7	5.017	—	36.31	5.9	5.199	—	38.62	14.2	3.2	[72]
$GdNi_3$	$PuNi_3$	5.009	—	24.57	2.0	5.182	—	24.81	8.1	2.4	[190]
$GdNi_3$	$PuNi_3$	5.009	—	24.57	3.0	4.944	—	31.41	23.0	4.5	[188]
$GdRh_2$	$MgCu_2$	7.514	—	—	3.2	4.80	5.10	9.50	9.6	1.6	[50]
$GdNi_4Al$	$CaCu_5$	4.969	—	4.048	3.5	5.169	—	4.142	11.1	2.8	[29]
Th_6Mn_{23}	Th_6Mn_{23}	12.40	—	—	23	13.02	—	—	15.8	3.3	[89]
$TbFe_2$	$MgCu_2$	7.341	—	—	*****	7.97	—	—	28.0	—	[52]
$TbFe_2$	$MgCu_2$	7.315	—	—	3.6	16.10	—	—	33.3	4.5	[185]
$TbFe_3$	$PuNi_3$	5.143	—	24.64	4.2	5.355	—	26.71	17.5	2.6	[71]
$TbCo_2$	$MgCu_2$	7.211	—	—	3.3	15.48	—	—	23.6	3.4	[61]
$TbCo_3$	$PuNi_3$	5.016	—	24.43	2.0	5.005	—	26.80	9.2	2.7	[70]
$TbCo_3$	$PuNi_3$	5.016	—	24.43	3.8	5.262	—	28.85	20.9	3.3	[70]
Tb_2Co_7	Gd_2Co_7	5.007	—	36.27	2.7	5.041	—	38.96	7.6	3.7	[72]
Tb_2Co_7	Gd_2Co_7	5.007	—	36.27	6.6	5.175	—	38.48	13.3	2.7	[72]
$TbNi_2$	$MgCu_2$	7.154	—	—	3.6	7.624	—	—	21.0	2.7	[185]
$TbNi_3$	$PuNi_3$	4.979	—	24.48	4.2	5.302	—	26.78	24.0	3.3	[190]
$TbNi_4Al$	$CaCu_5$	4.941	—	4.037	3.2	5.134	—	4.131	11.1	2.8	[29]
$DyMn_2$	$MgCu_2$	7.564	—	—	3.4	8.27	—	—	15.4	2.4	[65]
Dy_6Mn_{23}	Th_6Mn_{23}	12.36	—	—	23	12.90	—	—	13.6	2.8	[89]
$DyFe_2$	$MgCu_2$	7.309	—	—	3.4	7.94	—	—	28.2	4.0	[65]
$DyFe_3$	$PuNi_3$	5.116	—	24.55	1.8	5.26	—	25.54	10.0	3.4	[75]
$DyFe_3$	$PuNi_3$	5.116	—	24.55	2.5	5.34	—	25.80	14.5	3.6	[75]
$DyFe_3$	$PuNi_3$	5.130	—	24.52	3.0	5.31	—	26.59	16.2	3.3	[71]
$DyFe_3$	$PuNi_3$	5.116	—	24.55	4.2	5.36	—	26.46	18.0	2.7	[75]
$DyCo_2$	$MgCu_2$	7.187	—	—	3.4	7.721	—	—	24.0	3.3	[65]
$DyCo_2$	$MgCu_2$	7.191	—	—	3.7	7.759	—	—	25.6	3.2	[185]
$DyCo_3$	$PuNi_3$	5.007	—	24.27	2.1	4.992	—	26.61	9.0	2.5	[70]
$DyCo_3$	$PuNi_3$	5.007	—	24.27	3.7	5.233	—	26.66	20.0	3.2	[70]
Dy_2Co_7	Gd_2Co_7	4.988	—	36.15	2.6	4.984	—	38.70	6.9	3.4	[72]
Dy_2Co_7	Gd_2Co_7	4.988	—	36.15	6.4	5.169	—	38.31	13.8	2.8	[72]
$DyNi_2$	$MgCu_2$	7.149	—	—	2.0	7.551	—	—	17.8	4.1	[65]
$DyNi_2$	$MgCu_2$	7.150	—	—	3.5	7.58	—	—	19.2	2.5	[61]
$DyNi_3$	$PuNi_3$	4.980	—	24.44	2.2	5.039	—	26.67	11.9	3.1	[188]
$DyNi_3$	$PuNi_3$	4.980	—	24.44	3.4	5.280	—	26.74	23.0	3.9	[188]
$DyNi_4Al$	$CaCu_5$	4.928	—	4.038	*****	5.107	—	4.120	11.0	—	[29]
$HoFe_2$	$MgCu_2$	7.305	—	—	*****	7.73	—	—	15.5	—	[52]
$HoFe_2$	$MgCu_2$	7.291	—	—	3.6	15.82	—	—	27.7	3.7	[61]
$HoFe_3$	$PuNi_3$	5.177	—	24.48	3.6	5.316	—	26.39	16.4	2.8	[71]
Ho_6Fe_{23}	Th_6Mn_{23}	12.03	—	—	16	12.40	—	—	9.5	1.7	[191]
$HoCo_2$	$MgCu_2$	7.158	—	—	3.6	7.68	—	—	23.5	3.0	[61]
$HoCo_3$	$PuNi_3$	4.985	—	24.22	2.0	4.990	—	26.12	8.1	2.3	[70]
$HoCo_3$	$PuNi_3$	4.985	—	24.22	3.3	5.233	—	26.33	19.8	3.0	[70]
$HoNi_2$	$MgCu_2$	7.128	—	—	3.6	7.49	—	—	16.0	2.0	[61]
$HoNi_3$	$PuNi_3$	4.953	—	24.21	1.8***	4.991	—	26.12	9.6	3.0	[178]
$HoNi_3$	$PuNi_3$	4.963	—	24.28	3.6	5.305	—	26.70	20.4	4.1	[188]
$HoRu_2$	$MgZn_2$	5.244	—	8.810	4.2	5.65	—	9.33	22.9	2.9	[146]
$HoNi_4Al$	$CaCu_5$	4.919	—	4.037	*****	5.105	—	4.128	11.0	2.6	[29]
$ErMn_2$	$MgZn_2$	5.307	—	8.702	4.0	5.640	—	9.35	21.4	2.8	[41]
$ErFe_2$	$MgZn_2$	5.307	—	8.702	4.6	5.810	—	9.53	31.3	3.6	[41]
$ErFe_2$	$MgCu_2$	7.260	—	—	*****	7.91	—	—	29.3	—	[52]
$ErFe_2$	$MgCu_2$	7.269	—	—	3.0	15.73	—	—	26.6	4.3	[61]
$ErFe_2$	$MgCu_2$	7.269	—	—	3.9	7.82	—	—	25.0	3.1	[58]
$ErFe_2$ ******	$MgCu_2$	7.260	—	—	4.0	7.828	—	—	25.0	2.8	[66]
$ErFe_3$	$PuNi_3$	5.096	—	24.48	1.5	5.20	—	25.17	7.1	2.9	[74]
$ErFe_3$	$PuNi_3$	5.096	—	24.48	2.7	5.26	—	25.68	11.8	2.7	[74]
$ErFe_3$	$PuNi_3$	5.104	—	24.56	2.7	5.267	—	26.16	13.4	3.0	[71]
$ErFe_3$	$PuNi_3$	5.096	—	24.48	4.0	5.30	—	26.40	16.7	2.5	[74]
Er_6Fe_{23}	Th_6Mn_{23}	12.00	—	—	14	12.13	—	12.60	7.3	2.2	[191]
$ErCo_2$	$MgCu_2$	7.139	—	—	3.5	7.61	—	—	21.1	2.7	[61]

Table 3 (cont'd).

IMC	Structure type	Lattice parameters, A			H:M$_x$M'$_y$	Lattice parameters, A			$\Delta V/V_0$, %	ΔV/atoms of H, A^3	Refs.
		a	*b*	*c*		*a*	*b*	*c*			
$ErCo_3$	$PuNi_3$	4.977	—	24.26	1.8	4.981	—	25.83	6.6	2.1	[70]
$ErCo_3$	$PuNi_3$	4.977	—	24.26	3.6	5.223	—	26.27	19.3	3.1	[70]
$ErNi_2$	$MgCu_2$	7.108	—	—	3.1***	7.43	—	—	14.2	2.1	[40]
$ErNi_2$	$MgCu_2$	7.108	—	—	3.5	7.68	—	—	26.1	3.4	[61]
$ErNi_3$	$PuNi_3$	4.951	—	24.27	1.9	4.980	—	25.85	7.8	2.3	[190]
$ErRu_2$	$MgZn_2$	5.227	—	8.780	3.6	5.64	—	9.31	23.5	3.4	[46]
$ErNi_4Al$	$CaCu_5$	4.910	—	4.033	*****	5.096	—	4.122	11.0	—	[29]
$TmFe_2$	$MgCu_2$	7.252	—	—	3.0	15.44	—	—	20.6	3.3	[61]
$TmCo_2$	$MgCu_2$	7.122	—	—	3.7	7.600	—	—	21.5	2.6	[185]
$TmNi_2$	$MgCu_2$	7.095	—	—	3.6	7.52	—	—	19.1	2.4	[40]
$TmNi_3$	$PuNi_3$	4.935	—	24.26	2.0	4.983	—	25.85	8.6	2.4	[190]
$TmNi_4Al$	$CaCu_5$	4.900	—	4.026	*****	5.078	—	4.121	11.0	—	[29]
Yb_2Ru	*	—	—	—	6.0	7.248	—	—	—	—	[107]
$LuMn_2$	$MgZn_2$	5.227	—	8.537	*****	5.745	—	9.458	34.1	—	[42]
Lu_6Mn_{23}	Th_6Mn_{23}	12.21	—	—	*****	12.46	—	—	6.3	—	[42]
$LuFe_2$	$MgCu_2$	7.199	—	—	3.0	7.691	—	—	21.9	3.4	[185]
$LuCo_2$	$MgCu_2$	7.082	—	—	0.7	7.110	—	—	1.2	0.7	[185]
$LuCo_2$	$MgCu_2$	7.082	—	—	3.2	7.553	—	—	21.3	3.0	[185]
$LuNi_2$	$MgCu_2$	7.084	—	—	2.5	7.44	—	—	9.1	1.7	[40]
HfV_2	$MgCu_2$	7.37	—	—	4.0***	7.78	—	—	12.2	2.8	[144]
Hf_2Mn	Ti_2Ni	11.886	—	—	3.0	12.60	—	—	19.1	3.3	[82]
Hf_2Fe	Ti_2Ni	12.038	—	—	3.1	12.87	—	—	22.2	3.9	[82]
Hf_2Co	Ti_2Ni	12.071	—	—	3.6	12.74	—	—	17.6	2.7	[82]
HfCo	CsCl	3.164	—	—	3.2	3.485	10.35	4.267	21.4	2.1	[82]
Hf_2Ni	$CuAl_2$	6.395	—	5.240	3.1	6.740	—	5.608	18.9	3.3	[82]
HfNi	CrB	3.218	9.788	4.117	3.2	3.464	10.35	4.253	17.6	1.8	[82]
Hf_2Cu	$MoSi_2$	3.164	—	11.15	2.9	6.35	6.94	11.71	15.6	3.0	[100]
Hf_2Pd	$MoSi_2$	3.251	—	11.06	1.9	3.28	—	11.61	6.8	2.1	[100]
Hf_2Rh	Ti_2Ni	12.271	—	—	2.2	12.76	—	—	12.4	3.3	[82]
TaV_2	$MgCu_2$	7.14	—	—	1.7	7.34	—	—	8.6	2.3	[63]
Th_2Al	$CuAl_2$	7.616	—	5.861	4.0***	7.629	—	6.517	11.6	2.5	[165]
$ThTi_2$	*	—	—	—	6.0	9.124	—	—	—	—	[113]
$ThMn_2$	$MgZn_2$	5.478	—	8.941	*****	6.110	—	9.861	36.9	—	[42]
Th_6Mn_{23}	Th_6Mn_{23}	12.52	—	—	30	13.26	—	—	18.8	3.1	[57]
Th_7Fe_3	Th_7Fe_3	9.823	—	6.211	14.2	10.8	—	6.80	32.3	5.9	[93]
$ThZr_2$	*	—	—	—	7.0	6.176	—	10.085	—	—	[113]
ThNiAl	Fe_2P	7.078	—	4.053	3.0	7.340	—	4.228	12.2	2.4	[198]
$ThNi_2Al_2$	$CaCu_5$	5.127	—	4.120	2.7	5.217	—	4.183	5.0	1.8	[28]
UNiAl	Fe_2P	6.739	—	4.038	2.7	7.223	—	3.953	12.5	2.4	[198]

*The hydride phase is formed by high-temperature synthesis from two binary hydrides or from metal M' and the hydride of metal M in a hydrogen atmosphere.

**$\beta = 93.2°$.

***Data for deuterated specimens.

****$\beta = 97.0°$.

*****Composition of hydride phase not given in original work.

******$\alpha = 93.5°$.

The results presented suggest that the minimum radius for the hydrogen atom in metal hydrides is close to 0.2 Å. However, like other results suggesting that hydrogen can have an effective radius less than 0.2 Å (0.11 Å in the $LiPtD_{0.66}$ structure[160,161]), this requires careful experimental verification by carrying out more detailed and systematic structural researches.

The minimum H–H distances are either similar to or a little greater than the analogous distances in binary hydride structures. There is one exception, the Th_2AlD_3 structure[165], in which the presence of short H–H distances of length 1.66 Å was confirmed by n.m.r.

While this review was in the press a whole series of new papers on the structural chemistry of IMC hydrides[166–202] was published. The results of the most important of them are discussed briefly below.

The range of subjects for neutron-diffraction investigation has been broadened mainly through the study of new representatives of hydride phases formed on the basis of IMC's with structures belonging to the homologous series MM'_5–MM'_2 ($CaCu_5$ type—Laves phases). The deuterides $ZrVFeD_{3.6}$, $ZrVCuD_{4.0}$, and $ZrVNbD_{5.4}$ [166] based on IMC's with the $MgZn_2$ type structure are particularly interesting as the stoichiometric composition of the last of them is the maximum for hydrides based on the Laves phases. The tendency for preferential occupation of the $[hM_2M'_2]$ holes in the metal lattice was found to be maintained also in the structures of hydride phases richer in hydrogen than $ZrMoFeD_{2.6}$[138,139,167] and $ZrMn_2D_{3.0}$.[140] Thus in the $ZrVFeD_{3.6}$ and $ZrVNbD_{5.4}$ structures the $[hM_2M'_2]$ holes are occupied by up to 97% of the hydrogen atoms, and in the $ZrVCuD_{4.0}$ structure 89%. In addition a small number of hydrogen atoms are in $[hZrM'_3]$ holes, and for $ZrVCuD_{4.0}$ filling of the $[hM'_4]$ holes is also typical.

A comparison of all five ZrM'_2D_x structures based on IMC's with the $MgZn_2$ type structure which have been studied up to now shows that an equally probable distribution of hydrogen atoms in the $[hZr_2M'_2]$ holes does not occur in any of the structures. It is of interest that all the structures with $D/ZrM'_2 \leq 4.0$ are related to each other and may be regarded as derivatives of $ZrMoFeD_{2.6}$ which is the "poorest" in hydrogen: when the D/ZrM'_2 ratio exceeds 2.6, in addition to the two types of $[hZr_2M'_2]$ hole filled in $ZrMoFeD_{2.6}$, hydrogen atoms enter into two more types of hole in the metal sublattice different for each particular structure. The way in which the hydrogen atoms are distributed in the holes in the $ZrVNbD_{5.4}$ structure differs in principle from that in the other structures. There is a redistribution of the hydrogen atoms between two groups of $[hZr_2M'_2]$ holes in six-fold equivalent positions, as a result of which not only can the limiting composition $MM'_2H_{4.5}$ for the alternative model be exceeded without substantial distortion of the $MgZn_2$ type structure, but also the maximum stoichiometric composition $MM'_2H_{6-6.5}$ can be attained.

Returning to the results given in the main part of the review, we may conclude that an almost complete analogy exists between the structure of the hydride phases $MM'_2H(D)_x$ based on IMC's with $MgCu_2$ and $MgZn_2$ type structures: at low hydrogen concentrations only the $[hM_2M'_2]$ holes are filled, and on increasing the hydrogen content the preference for filling these holes is retained, but hydrogen atoms are also inserted into holes with a smaller content of metal M, in the $[hMM'_3]$ holes in the first place.

Several recent publications[168–170] are devoted to hydrides based on MM'_5 compounds with the $CaCu_5$ type structure.

The structure of the mixed oxyhydride phase $Ti_4Fe_2.OD_{2.25}$ [171] (the parent IMC Ti_2Fe crystallises in the Ti_2Ni type only in the presence of oxygen) is of undoubted interest. The presence of chemisorbed oxygen in the lattice must indicate fairly definitely the choice of positions for the introduction of hydrogen atoms. As with the shortest H–H interatomic distances characterising the "blocking radius" of neighbouring holes, an analogous value can also be determined for the O–H(D) contacts. The experimentally determined value $d_{O-D} = 1.68$ Å for the $Ti_4.Fe_2OD_{2.25}$ structure, as expected, substantially exceeds the value 0.96 Å typical of an O–H covalent bond in the water molecule, and lies in the typical range for the length of O...H hydrogen bonds, which undoubtedly indicates a definite interaction between the oxygen and hydrogen atoms.

Three types of hydrogen atom in the structure occupy two different types of hole, their coordination polyhedra being the octahedron $[D^{(1)}Ti_6]$ and the tetrahedra $[D^{(2)}.Ti_3Fe]$ and $[D^{(3)}Ti_3Fe]$, as atoms $D^{(2)}$ and $D^{(3)}$ occupy the same type of hole. The crystallographic positions, which these atoms can occupy inside a specific hole, are within a sphere of diameter ~0.3 Å.

A characteristic feature of IMC hydrides is that they are, as a rule, non-stoichiometric and that in their structures there is a statistical distribution of hydrogen atoms in crystallographic positions, with the number of positions substantially exceeding the number of inserted atoms. When the temperature is reduced, owing to the non-zero configurational entropy, phase transitions of the order-disorder type[172,173] must take place, leading to removal of the "degeneracy" of the equivalent holes—some of them are filled in an ordered way, and the remainder become vacant. In addition to $ZrV_2D_{3.7}$ [145] and $HfV_2D_{4.0}$ [144] discussed above, such transitions were observed as the temperature is lowered in Sr_2IrD_5.[174] The order-disorder phase transition in the last case is accompanied by a lowering of the lattice symmetry from cubic to tetragonal and a reduction in the deuterium atom occupation factor of each of five Sr_4Ir pyramids ($n = 0.70$), while the occupation factor of the remaining [hSr_4Ir] holes is close to the possible limit ($n = 0.96$). A similar phase transition on reducing the temperature also takes place in a hydride phase based on the IMC Y_6Mn_{23} [175]—here the lattice symmetry is lowered from cubic (space group $Fm3m$) to tetragonal ($P4_2/mnm$).

X-Ray diffraction studies, like neutron-diffraction work, have been carried out mainly for hydride phases based on IMC's with Laves phase and $CaCu_5$ type structures. A study of the process of hydrogenation and subsequent dehydrogenation of $CaNi_5$, carried out under conditions of equilibrium saturation of specimens with hydrogen directly in the course of the X-ray diffraction experiment[176], showed the presence of three hydride phases, α' ($CaNi_5H_{0.8-1.2}$), β ($CaNi_5H_{4.5-5.6}$), and γ ($CaNi_5H_{6+x}$), whose symmetry changes from hexagonal to orthorhombic and again to hexagonal (trigonal) as the hydrogen content in the hydride is increased. Data on the existence of $CaNi_5H_5$ with an orthorhombic structure had been obtained independently and previously[177].

For hydrides based on the alloys $LaNi_{5-x}Fe_x$ [178] the hexagonal symmetry of the IMC is retained.

Among Laves phase hydrides studied in the most detail are alloys, whose composition corresponds to the quasi-binary section MM'_2–MM''_2, namely $Zr(Cr, Fe)_2$, $Zr(Cr, Co)_2$,[179] $Tb(Co, Fe)_2$, $Dy(Co, Fe)_2$,[180] $Zr(Mn, Fe)$,[181] $Zr(V, Fe)_2$, $Zr(V, Cr)_2$,[182] $Ti(Be, Cu)_2$,[183] $Ho(Co, Fe)_2$ and $Er(Co, Fe)_2$.[184] The systematic investigation of the hydrides MM'_2H_x (M = lanthanide, M' = Fe, Co, Ni) has also been continued[185–187]. It was found that the original symmetry of the unit cells of the IMC structures is retained and their volume increases by $\Delta V \sim 2.5$ Å^3 for each H atom.

Systematic researches on the hydrides MM'_3H_x (M = Y, Gd, Dy, Ho; M' = Ni, Co),[188–190] based on IMC's with the $PuNi_3$ type structure, and also $M_6M'_{23}H_x$ (M = Y, Sm, Gd, Ho, Er; M' = Mn, Fe) [191,192] (parent IMC's of the Th_6Mn_{23} type) have been continued. The results confirmed earlier conclusions as to the crystallographic characteristics of the hydride phases in the related systems MM'_3–H_2 [70–72] and $M_6M'_{23}$–H_2.[87–89] Similar conclusions can be drawn for the hydrides based on the alloys $TiFe_{1-x}M'_x$, where M' = Al, Cr, Mn, Co, Ni.[193,194] The structure and properties of hydrides based on IMC's of titanium have been investigated[195,196]. A re-examination of the structural phase transitions in Mg_2NiH_4 [197] is in agreement with earlier results[102,103].

The reaction of the compounds UNiAl and ThNiAl with hydrogen has been investigated[198]. These compounds belong to the Fe_2P structure type, which can be regarded as a packing of trigonal prisms and is in this sense similar to one of the structure types whose reaction with hydrogen was studied previously, namely CrB. The hexagonal unit cells of the parent intermetallic compounds behave differently on hydrogenation: in ThNiAl the expansion is practically isotropic and fairly small ($\Delta a/a_0 \sim \Delta c/c_0 \sim 0.04$), whereas the UNiAl structure is "compressed" in the z axis direction and substantially expanded in the basal plane ($\Delta a/a_0 \sim 0.07$).

In addition to neutron and X-ray diffraction experimental researches, work has been published in which, by identifying all possible types of hole in the metal matrix, the most probable models for the structure of hydride phases based on IMC's crystallising in the Th_6Mn_{23} [199] and CrB types[200] have been considered. The most probable models for the structure of the hydrides $MM'H_x$ (CrB parent type) and MM'_3H_x ($PuNi_3$ parent type) have been discussed in connection with elucidation of the structure of $HoNi_3D_{1.8}$.[202]

There is also a review in the field of binary hydride structural chemistry[203] giving results on the synthesis of transition-metal hydrides by direct reaction of the metals with hydrogen at high hydrogen pressures and on their properties. This synthetic method has recently permitted the range of "hydrogenated" metals to be extended to gold, which forms a hydride of approximate composition $AuH_{0.4}$ with an orthorhombic structure[204].

Thus, in the structures of complex metal hydrides studied up till now the hydrogen atoms most frequently have a c.n. of 4 or 6 with tetrahedral or octahedral coordination, more rarely a c.n. of 3 or 5, but linear coordination is observed only for two structures. In most cases there is no reorganisation of the IMC structure when hydrogen atoms are introduced into their lattices.

Of the different types of hole in the metal lattice, those filled first in the hydrides are those surrounded by the greatest number of atoms of the metal M. This rule is general for metal hydride structures and can be explained by the simultaneous effect of a number of factors: (1) the activity of metal M on reaction with hydrogen; (2) the greatest effective size of these holes of all those present in the metal lattice; (3) the M–M distances in the periphery of the holes occupied by hydrogen atoms exceed the sum of the corresponding metal radii, so that these holes are the most easily deformed when the hydride phases are formed.

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New Problems and Prospects in the Electrochemistry of Semiconductors

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This review gives a unified discussion of current theoretical ideas in semiconductor electrochemistry and in the interpretation of physicochemical processes at the semiconductor/electrolyte interface (mainly, the electrochemical phenomena associated with the photo-excitation of the electron-hole ensemble of the semiconductor and used in practical devices for solar energy conversion, laser etching of semiconductors, photo-corrosion protection, etc.). New problems and likely future developments in the electrochemistry of semiconductors are discussed. 90 references.

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I. INTRODUCTION

The electrochemistry of semiconductors, identified as a new branch of science over a quarter of a century ago, has been developed intensively as a part of electrochemical physics† since the 1960's. Its scientific foundations were laid, and new methods of treating semiconductor surfaces were developed and adopted in the technology of semiconductor devices[1]. The results stimulated a reconsideration of the most general electrochemical concepts, such as the zero-charge potential, the exchange current, the transfer coefficient of an electrochemical reaction, etc. This was followed by a period of decreasing interest in semiconductor electrochemistry, mainly because the practical applications were found to be more limited than had been expected.

The resurgence of research activities in this area, which is still in progress, arose from the discovery (in the 1970's) of solar energy conversion by the photo-electrolysis of water with semiconductor electrodes to give hydrogen. Partly because of the increasing concern with the danger of exhausting natural resources, and partly with the aim of minimising the contamination of the environment, substantial effort has been directed[2] towards the development of ecologically "clean" liquid solar cells which exploit renewable sources of energy. Practical developments in "solar semiconductors" gave a new impetus to the study of semiconductor electrochemistry (mainly, the photo-electrochemistry of semiconductors). In their turn, advances in semiconductor electrochemistry stimulated new developments in conventional electrochemistry. For example, the study of semiconductor electrodes has led to a critical reappraisal of general concepts such as the electrochemical potential of electrons in solution, the relationship between the "physical" energy scale and the "electrochemical" scale of electrode potentials, etc. These problems will be examined in the first part of the present review.

In the later Sections we shall discuss some new problems in the electrochemistry (and photo-electrochemistry) of the semiconductors themselves, such as the "clamping of the Fermi level" on the surface of a semiconductor electrode (as an alternative to the more usual "clamping of the band edges"), the quasi-thermodynamic description of electrode reactions (in particular, the concept of the quasi-Fermi level, and its limitations), etc. We shall also briefly outline the principles of some very recent practical developments in the electrochemistry of semiconductors.

For information on the physics of semiconductors and semiconductor surfaces the reader is referred to Bonch-Bruevich and Kalashnikov's monograph[3]; general problems in semiconductor electrochemistry are discussed in Refs.1, 4, and 5. A more detailed and comprehensive discussion of some of the problems mentioned in this review is given in our textbook[6].

II. CHARACTERISTIC ENERGY LEVELS IN THE ELECTRODE–ELECTROLYTE SOLUTION SYSTEM

The description of the energy characteristics of electrons in electrochemical systems is of the greatest importance both in method development and in practical terms. The concept of the electrochemical potential of electrons in a solution containing an oxidation–reduction system is valuable when applied to electrochemical and photo-electrochemical processes. Also, the reorganisation energy of the solvent can substantially affect the kinetics of the reactions which accompany the charge transfer act. Lastly, the electronic energy levels, directly related to the oxidation or reduction state of the components, determine the quantitative aspects of the related electron flows.

1. The Electrochemical Potential of Electrons in a Solution

Consider an electron in a solution which contains an oxidation–reduction system taking part in a reversible electron transfer reaction:

$$\mathrm{Ox} + n\,\mathrm{e}^- \rightleftarrows \mathrm{Red}\,. \qquad (1)$$

In this expression Ox and Red denote the oxidised and the reduced form of the substance in the solvated state, and n is the number of electrons involved in the electrode reaction. Under conditions of thermodynamic equilibrium we must have

$$\tilde{\mu}_{ox} + n\tilde{\mu}_e = \tilde{\mu}_{red} \qquad (2)$$

where $\tilde{\mu}_{\mathrm{ox}}$ and $\tilde{\mu}_{\mathrm{red}}$ are the electrochemical potentials of the components of the oxidation–reduction system in the solution

†The term "electrochemical physics" was officially adopted by the International Electrochemical Society to denote all the aspects of electrochemistry which have strong associations with physics.

(referred to one mole of substance), and $\tilde{\mu}_e$ is the electrochemical potential of the electrons in the solution. We can define the quantity $\tilde{\mu}_{ox,red}$ as

$$\tilde{\mu}_{ox,red} = RT \ln c_{ox,red} + z_{ox,red}\mathcal{F}\emptyset + \mu^0_{ox,red} \qquad (3)$$

where R is the gas constant, T is the absolute temperature, $c_{ox,red}$ is the concentration (more generally, the activity) of the reactants Ox and Red in solution, $z_{ox,red}$ are their charges, $\mathcal{F}$ is the Faraday, $\emptyset$ is the electrical potential, and $\mu^0_{ox,red}$ are constants independent of $c_{ox,red}$ and of $\emptyset$.

From (2) and (3) we can calculate the equilibrium electrode potential ϕ^0 of an electrode on which reaction (1) is taking place:

$$\varphi^0 = \varphi^0_0 + \frac{RT}{n\mathcal{F}} \ln \frac{c_{ox}}{c_{red}} \qquad (4)$$

where ϕ^0_0 is the standard electrode potential for the given solution. This quantity depends on the difference $\mu^0_{ox} - \mu^0_{red}$, and therefore also on the nature of the electrode reaction and on the choice of reference electrode.

At the same time, when thermodynamic equilibrium according to reaction (1) has been established we can introduce the concept of the electrochemical potential of electrons in the electrolyte solution, $\tilde{\mu}^{el}_e$, which is quite unrelated to the presence (or absence) of the electrode. This possibility follows from the general thermodynamic principle that the detailed mechanism by which an equilibrium is established is immaterial. Thus we can, for example, assume that the electron transfer reaction between the Ox and the Red component does not in general involve the participation of the electrode. Under these conditions the quantity $\tilde{\mu}^{el}_e$ for reaction (1) is given by the expression

$$\tilde{\mu}^{el}_e = \frac{1}{n}(\tilde{\mu}_{red} - \tilde{\mu}_{ox}) \qquad (5)$$

where $\tilde{\mu}_{red}$ and $\tilde{\mu}_{ox}$ are defined for the potential $\emptyset$(el) in the bulk of the electrolyte solution. Since the parameters $\tilde{\mu}_{red,ox}$ are a function only of the properties of the reactants Ox and Red and of the solvent, it follows that $\tilde{\mu}^{el}_e$ also is independent of the nature of the electrode and of the structure of the phase boundary. Furthermore, it is the quantity $\tilde{\mu}^{el}_e$ which defines the electrochemical potential of the electrons in the given electrode at equilibrium. In particular, this electrochemical potential must be the same for any electrode in equilibrium with the given Ox/Red system.

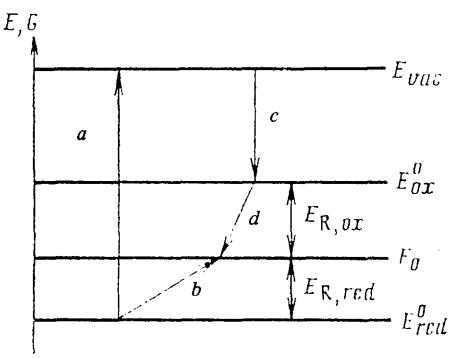


Figure 1. Position of the energy levels of an electron in a solution containing an oxidation–reduction system: E is the internal energy, G is the free energy.

To establish the relationship between μ^{el}_e and the characteristic parameters of the oxidation–reduction system we shall consider a solution containing only one particle of Red. We shall denote the most probable (thermodynamic) electronic energy level of the Red particle as E^0_{red}, and that of an Ox particle as E^0_{ox}, and the potential energy of an electron in vacuum (or, more exactly, in the vapour phase) at a point close to the surface of the solution but outside the region of influence of the surface forces will be termed E_{vac}. If the surface is uncharged the parameter E_{vac} is the same as the energy of an electron at rest at infinity. Putting $n = 1$ in Eqn.(1) to simplify the argument, we can now examine the following thermodynamic cycle[7,8] (see Fig.1).

a) An electron is transferred in a single jump from a solvated Red particle (energy level E^0_{red}) to the level E_{vac}.

b) The state of the solvent near the oxidised Red particle (now an Ox particle) is changed to bring the Ox particle into thermodvnamic equilibrium with the solution.

c) The electron from the level E_{vac} is suddenly transferred to the resulting Ox particle (level E^0_{ox}) without changing the state of the solvent.

d) The necessary rearrangement of the solvent near the resulting Red particle is carried out, and as a result the system as a whole returns to its initial equilibrium state.

In this cycle the changes in internal energy of the system corresponding to steps (a) and (c) are a measure of the position in energy of the levels E^0_{red} and E^0_{ox} relative to E_{vac}: they are equal to the ionisation energy of the Red particle and to the electron affinity of the Ox particle in the solution respectively. The energy characteristics of steps (b) and (d) are the reorganisation energies of the solvent $E_{R,red}$ and $E_{R,ox}$ for the particles Red and Ox respectively.

In this process $E_{R,red} > 0$ and $E_{R,ox} > 0$ are the absolute measures of the energy (or, more accurately, of the free energy) needed to change the equilibrium state of the medium (solvent) from its initial state to the final state for a unit change in the charge on the particle[9,10].

Thus according to the above analysis we can write

$$E^0_{red} + E_{R,red} - E^0_{ox} + E_{R,ox} = 0. \qquad (6)$$

The quantity F_0, defined according to Eqn.(6) by the expression

$$F_0 = E^0_{red} + E_{R,red} = E^0_{ox} - E_{R,ox} \qquad (7)$$

is a measure of the change in free energy of the system accompanying the removal (at equilibrium) of an electron from a Red particle from the solution into the vacuum (or the equilibrium transfer of an electron from the vacuum to an Ox particle). From (6) and (7) we obtain

$$F_0 = \tfrac{1}{2}(E^0_{ox} + E^0_{red}) + \tfrac{1}{2}\Delta E_R \qquad (8)$$

where

$$\Delta E_R = E_{R,red} - E_{R,ox}$$

and

$$E^0_{ox} - E^0_{red} = E_{R,ox} + E_{R,red}. \qquad (9)$$

We note that Eqn.(9) can be obtained also by considering the equilibrium transfer of an electron directly from the reactant Red to the reactant Ox within the solution.

In polar liquids like water (especially in the case of outer-sphere reactions[11]) we can assume that $E_{R,ox} = R_{R,red} = E_R$. From Eqns.(8) and (9) we then obtain

$$F_0 = \tfrac{1}{2}(E^0_{ox} + E^0_{red}), \quad E^0_{ox} - E^0_{red} = 2E_R. \qquad (10)$$

It follows therefore that in the simplest case (which we are now considering) the characteristic level E_0 lies half-way between E^0_{ox} and E^0_{red} in energy, and the distance in energy between E^0_{ox} and E^0_{red} is twice E_R.

Thus, starting from (3) and (5), and noting that the parameter F_0 as defined above relates to one particle, we obtain the following expression for the electrochemical potential $\tilde{\mu}_e^{el}$:

$$\tilde{\mu}_e^{el} = N_A F_0 - RT \ln (c_{ox}/c_{red}) \qquad (11)$$

where N_A is Avogadro's number. Eqn.(11) can be obtained also by statistical mechanics[6,8] without using Eqn.(5) and without carrying out the thermodynamic cycle. In other words, the concept of the electrochemical potential of electrons in a solution can be introduced strictly and logically in both the thermodynamic and the statistical mechanics approach.

By analogy with the Fermi level of the electron in solids, which refers to a single electron, we can define the quantity $F_{redox} = \tilde{\mu}_e^{el}/N_A$ as the electrochemical potential of the electrons in solution referred to a single particle (sometimes loosely called the Fermi level of the electrons in solution).

We should stress that the position of F_{redox} is quite unrelated to the concentration of "free" electrons in solution, and is determined by the properties of the oxidation–reduction Ox/Red system (which contains only "bound" electrons). The quantity F_{redox} does not describe the energy of any one particle, since in general there are no electrons of energy F_{redox} in the solution (in contrast to metal systems, say, where the Fermi level F_{met} coincides with the energy of the conduction electrons on the Fermi surface). Therefore during an electrochemical reaction the electrons are not transferred from the level F_{redox} to the electrode or from the electrode to F_{redox}: all the electron transfers take place through the levels E_{red}^0 and E_{ox}^0. Nevertheless it is the position of the level F_{redox} which defines the thermodynamic properties of the oxidation–reduction system, and also the properties of the interface between the electrode and the solution which contains the system. For example, using the condition of thermodynamic equilibrium in the semiconductor–solution system in the form of

$$F = F_{redox} \qquad (12)$$

where F is the Fermi level of the electrons in the semiconductor, the conditions which determine the course of the electrochemical reaction can be defined as

$$F > F_{redox} \quad \text{(cathodic reaction)}, \qquad (13a)$$

$$F < F_{redox} \quad \text{(anodic reaction)}. \qquad (13b)$$

The electrochemical potentials of oxidation–reduction systems in solution can be calculated by standard methods from the thermodynamic characteristics of the components. For many reactions in which the material of the semiconductor electrode takes part (for example, anodic or cathodic dissolution) the F_{redox} values can be found in Refs.12–14.

2. Relationship Between the Energy Scale and the Electrode Potential Scale

The position of the levels E_{ox}^0, E_{red}^0, and F_{redox} with respect to E_{vac} can be defined by establishing a quantitative correspondence between the "physical" energy scale, in which the zero value is identified with E_{vac}, and the electrochemical scale of electrode potentials, which are measured from the potential of some arbitrarily chosen reference electrode. The general form of this correspondence is

$$F_{redox} = -e\varphi^0 + \text{const} \qquad (14)$$

where $e > 0$ is the absolute value of the electronic charge.

Let us choose an Ox/Red system for which the equilibrium potential ϕ^0 is arbitrarily taken to be zero. A solution of this system in contact with an inert electrode [i.e. one which does not take part in reaction (1)] is by definition the reference electrode. In this case the constant in Eqn.(14) is equal to F_{redox}, and describes the change in free energy attending the reaction

$$Ox + e_{vac}^- \rightleftarrows Red. \qquad (15)$$

In other words, the term "const" in Eqn.(14) is the change in free energy resulting from the transfer of an electron from a point in the vacuum close to the solution surface to the Fermi level of the metal of the reference electrode (which is equal to F_0 when $c_{ox} = c_{red}$). The quantity F_0/e is sometimes called the "absolute potential" of the electrode[15]. The first attempt to determine this quantity was described by Kanevskii[15]; Lohmann also calculated it by analysing a fairly complex thermodynamic cycle[16].

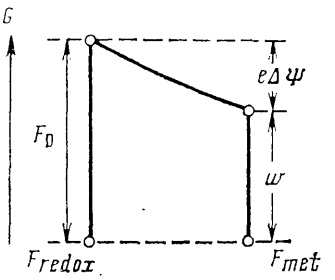


Figure 2. Relationship between the "physical" and the "electrochemical" energy scale.

A simple and accurate method of comparing energy and potential scales[17] relies on a calculation of the electronic work function for the metal in a solution of electrolyte at the potential of the reference electrode. The metal in equilibrium with the Ox-Red system in solution (so that their electrochemical potentials are equal, $F_{redox} = F_{met}$) is shown diagrammatically in Fig.2. The change in free energy for the reaction (15) is the sum of the energies for the steps (c) and (d) of our cycle (Fig.1), i.e. the quantity F_{redox}. We see from the cycle in Fig.2 that

$$-F_{redox} = w + e\Delta\psi \qquad (16)$$

where w is the thermodynamic work function for the emission of an electron from the uncharged metal into a vacuum and $\Delta\psi$ is the Volta potential difference in the metal–solution system produced by the mutual charging of the "free" metal and solution surfaces when brought into contact.

A calculation for a specific case (for example, the normal hydrogen electrode) is easily made by using data[18] for the difference in Volta potentials in the mercury–aqueous solution system: $\Delta\psi = -0.07$ V at the potential of the normal hydrogen electrode. Taking $w = 4.50 \pm 0.03$ eV for the work function of an electron from mercury into a vacuum[19] we obtain from formula (16)

$$-F_{redox}\,(\text{NHE}),\ \text{eV} \quad = 4.50 - 0.07 = 4.43 \simeq 4.4\,.$$

Thus the electrochemical potential of the normal hydrogen electrode F_{redox}(NHE) lies 4.4 eV below the level E_{vac}.[6]

We also note that w (the thermodynamic work function of the electron in the semiconductor) is given by the expression $w = \chi + |F - E_c|$, where χ is the electron affinity of the semiconductor. The position of the level F with respect to the bottom of the conduction band in the bulk of the semiconductor (E_c) is given by the expressions

$$F - E_c = -E_g/2 + kT \ln (N_v/N_c)^{1/2}, \quad n_0 = p_0 \qquad (17a)$$
(intrinsic semiconductor)

$$F - E_c = -kT \ln (N_c/n_0), \quad n_0 \gg p_0 \qquad (17b)$$
(*n*-type semiconductor)

$$F - E_c = -E_g + kT \ln (N_c/p_0), \quad p_0 \gg n_0 . \qquad (17c)$$
(*p*-type semiconductor)

In these expressions E_g is the width of the forbidden gap, N_c and N_v are the effective densities of states in the conduction band and in the valence band, and n_0 and p_0 are the concentrations of electrons and holes in thermodynamic equilibrium in the bulk of the semiconductor.

3. Calculation of the Reorganisation Energy of the Solvent

By using these results we can calculate the reorganisation energy of the solvent from data on the photo-emission of electrons from solutions into the vapour phase (see our recent review[20]). When a solution containing "Red" species is illuminated with light of sufficiently short wavelength electrons are emitted into the vapour phase. Since photo-ionisation is a relatively fast process, the photo-electric work function w_{ph} is equal to $-E^0_{red}$ if $E_{vac} = 0$. It follows from (7) and (11) that for $c_{ox} = c_{red}$ this quantity differs from the thermodynamic work function (which is equal to F_0) by the amount $E_{R,red}$. Thus $E_{R,red}$ is calculable as the difference between the photo-electric work function $w_{ph} = -E^0_{red}$ and the parameter $-F_{redox}$. (A similar method of determining E_R was used previously[21] for solutions in which the "emitters" were solvated electrons.)

The work function $w_{ph} = 5.95$ eV has been obtained[22] for photo-emission from aqueous solutions of $Fe(CN)_6^{4-}$. Using the above value of $F_{redox} = -4.4$ eV, and also a value of +0.36 V (against the normal hydrogen electrode) for the standard potential of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ system, we obtain 5.95 - 4.4 - 0.36 ≅ 1.2 eV for the reorganisation energy of the water surrounding the ferrocyanide and ferricyanide ions. Since in this case the electron transfer reaction takes place in the outer sphere we can assume that $E_{R,ox} = E_{R,red} = E_R$.

Few reliable experimental data on E_R are available at present[9]. According to Memming[23] the $E_{R,ox}$ and $E_{R,red}$ values for aqueous solutions at room temperature lie between 0.5 and 2 eV. We should also note that the "homogeneous" values of E_R (determined, for example, by photo-electron emission from solutions) are substantially higher than the "heterogeneous" values (which can be obtained from measurements of tunnelling currents from semiconductor electrodes into solutions[23]). In the simplest model the "homogeneous" reorganisation energy of the solvent is approximately double the "heterogeneous" value[9,11].

As regards the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ system, the "homogeneous" value $E_R = 1.24$ eV obtained by a model calculation[23] agrees very well with the value given above. However, the same workers[23] obtained a much lower value for the "heterogeneous" reorganisation energy of the solvent ($E_R = 0.4$ eV) from experimental measurements of tunnelling currents from heavily doped SnO_2 electrodes.

III. STRUCTURE OF THE SEMICONDUCTOR/ELECTROLYTE INTERFACE

At the interface between a semiconductor electrode and a solution of electrolyte an electrical double layer is produced (as at the metal/solution interface). The double layer consists of regions carrying charges of opposite sign, and located in the two contacting phases. In the semiconductor the charge in the surface layer is produced by a redistribution of the electrons and holes present in this region, and in the solution by a redistribution of the ions. At equilibrium the absolute values of these charges are equal.

1. Model of the Electrical Double Layer

The fundamental reasons for the formation of an electrical double layer are quite general. They include the overflow of charges through the interface during the establishment of thermodynamic equilibrium between the phases, and charging processes which are independent of the transfer of electrons through the interface (for example, the charging of surface states, some types of adsorption, etc.).

According to the generally accepted model[1,24] we can define three regions within the electrical double layer: a region of space charge in the solution, an intermediate region (usually called the Helmholtz layer), and a region of space charge in the semiconductor.

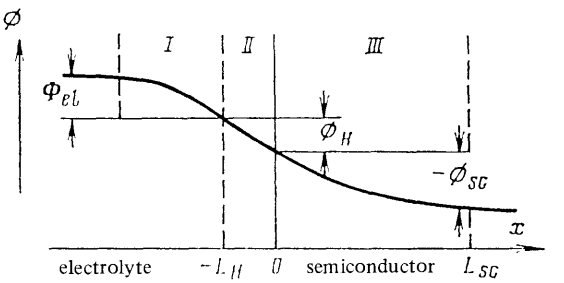


Figure 3. Composition of the potential step at the semiconductor–electrolyte interface: *I*) Gouy layer, *II*) Helmholtz layer, *III*) space-charge layer.

The distribution in space of the potential difference at the interface (Galvani potential) between a semiconductor and an electrolyte, Ø(el/sc), is shown in Fig.3. The semiconductor occupies the space to the right of the vertical full line which defines the interface ($x = 0$). To the left of this line we find the Helmholtz layer, consisting of ions attracted towards the electrode surface and of solvent molecules: the thickness of this layer (L_H) is of the order of the diameter of the ions. Beyond the Helmholtz layer we find, on the solution side, the space-charge region of the solution (the Gouy–Chapman layer).

We shall denote the electrical potential in the bulk of the semiconductor (at $x \to \infty$) as Ø(sc), and in the bulk of the solution (at $x \to -\infty$) as Ø(el), as before. The overall potential drop at the interface, Ø(el/sc) = Ø(sc) - Ø(el), is therefore given by

$$Ø(el/sc) = [Ø(L_H) - Ø(-\infty)] + [Ø(0) - Ø(L_H)] + [Ø(\infty) - Ø(0)], \qquad (18)$$

In this expression $\emptyset(L_H) - \emptyset(-\infty) \equiv \emptyset(el)$ is the potential drop in the space-charge region of the electrolyte solution, i.e. between the bulk of the solution and the outer Helmholtz plane: this quantity is usually called ψ' (the "psi-dash" potential). The second term $\emptyset(0) - \emptyset(L_H) \equiv \emptyset_H$ is the potential drop in the Helmholtz layer. Lastly, the third term $\emptyset(\infty) - \emptyset(0) \equiv -\emptyset_{sc}$ is the potential drop in the space charge region of the semiconductor.

We must lay special stress on the following consideration. In electrochemistry an electrode potential is traditionally taken as positive if it increases the amount of positive charge on the electrode. On the other hand in semiconductor physics a positive surface potential [conventionally measured from $\emptyset(\infty)$] corresponds to electron enrichment of the space charge region, i.e. to the formation of negative space charge. In other words, the potential axes adopted in electrochemistry and in semiconductor physics point in opposite directions. The result is that the potential step in the semiconductor with respect to the bulk potential $\emptyset(sc)$, defined as $\emptyset(sc) = \emptyset(0) - \emptyset(\infty)$, has a sign opposite to that of the last term in the expression for the Galvani potential [Eqn.(18)].

Polarisation of the electrode, i.e. a change by $\Delta\phi$ in the electrode potential, usually affects all three components of the Galvani potential. However, in the not too dilute solution (>0.1 M) which are usually used in electrochemical experiments the quantity $\emptyset_{el} = \psi'$ is negligibly small, and therefore the changes in this quantity are also negligible. We shall assume this to be the case throughout this review. We shall also assume that the ohmic potential drop is negligible, so that we can write

$$\Delta\varphi = \Delta\emptyset_H - \Delta\emptyset_{sc}. \qquad (19)$$

In addition to the charge carriers, dipoles present at the interface can also contribute to the formation of the double layer: these dipoles could be the surface dipoles accompanying bond formation between atoms on the semiconductor surface and atoms adsorbed from the solution, or surface dipoles produced by the oriented adsorption of solvent molecules.

The formation of an array of dipoles does not contribute to the charge on the electrode, but it produces an additional potential step included in the parameter $\emptyset_H$. This step ($\emptyset_{H,dip}$) is usually found experimentally to be relatively insensitive to changes in the electrode potential ϕ, but very sensitive to the previous treatment of the electrode surface and to the composition of the surrounding medium.

A dependence of the potential on the coordinate in the semi-conductor [$\emptyset(x)$] is equivalent, in the band model, to a bending of the energy bands. The bending is downwards if $\emptyset_{sc} > 0$, and upwards of $\emptyset_{sc} < 0$. In the latter case, corresponding to electron depletion in the surface layer, a depletion layer (the Mott–Schottky layer) is formed near the interface of *n*-type semiconductors if the following inequality applies:

$$-\frac{kT}{e}\ln\frac{n_0}{p_0} < \emptyset_{sc} < -\frac{kT}{e} \qquad (20a)$$

The space charge in this case consists mainly of ionised impurity donors, present at a concentration $N_D \cong n_0$. Similarly, on *p*-type semiconductors the charge of the depletion layer produced by downward bending of the bands in the potential region

$$\frac{kT}{e} < \emptyset_{sc} < \frac{kT}{e}\ln\frac{p_0}{n_0} \qquad (20b)$$

consists mainly of acceptor impurities containing trapped electrons (present at a concentration $N_A \cong p_0$).

The formation of a depletion layer is the most important case in practice, since in the wide-band doped semiconductors used in modern semiconductor electrochemistry experiments the potential range defined by the expressions (20) is quite wide.

If $\emptyset_{sc} = 0$ the bands remain "flat" up to the interface. In this case the space charge in the semiconductor is zero. The potential ϕ of the semiconductor electrode measured against some reference electrode and corresponding to the condition $\emptyset_{sc} = 0$ is called the flat band potential $\phi = \phi_{fb}$. The flat band potential in the electrochemistry of semiconductors is equivalent to the zero-charge potential in the electrochemistry of metals (more precisely, to the zero free charge potential[25]), and it plays an important role in the kinetics of electrochemical processes on semiconductor electrodes.

We should note that for $\phi = \phi_{fb}$, though $\emptyset_{sc} = 0$, the parameter $\emptyset_H$ is finite (usually as a reult of the specific adsorption of ions from solution). Thus in the case of oxide semiconductors (TiO_2, ZnO, etc.), or of semiconductors whose surface is oxidised in aqueous solutions (for example, Ge), the concentrations of OH^- and H^+ ions chemisorbed on the surface are not equal, and this effect can made a substantial contribution to $\emptyset_H$. Because of the thermodynamic equilibrium between the ions adsorbed on the surface and those in the bulk of the solution this contribution to $\emptyset_H$ should be a linear function of the pH of the solution. At a pH value depending on the nature of the semiconductor electrode the total charge of the adsorbed ions is zero. This pH value (or the analogous parameter for the adsorption of ions other than hydrogen), called the point of zero zeta-potential or the isoelectric point, is equivalent to a zero total charge potential for the condition $\emptyset_{sc} = 0$ in Rzhanov's terminology[26]. We note that even at the isoelectric point the parameter $\emptyset_H$ is usually different from zero as a result of adsorption of dipolar solvent molecules at the interface, and also (in the case of oxidised semiconductors) because of the polarity of the bond between the semiconductor atom and the oxygen.

Electronic surface states (including interfacial states) play an important role in semiconductor electrode processes. Adsorbed particles and defects are always present at the contact between the semiconductor and the solution. As a result, a real semiconductor surface contains different types of electronic level, characterised by a complex (usually, quasi-continuous) energy spectrum, at concentrations which can be as high as 10^{14} cm^{-2}. For a more detailed discussion of these aspects the reader is referred to Refs.26 and 27.

The existence of electronic surface levels causes two very important effects. Firstly, electrons and holes can be trapped at the surface, forming an electric charge which induces an equal and opposite charge in the bulk. This effect is responsible for the influence of the surface on the equilibrium properties of the semiconductor. Secondly, surface levels can radically influence the kinetics of processes involving electrons and holes, partly by providing additional carrier recombination and generation centres and partly by acting as intermediate energy levels in processes involving charge transport through the phase boundary.

2. Potential Distributions. "Clamping" of the Band Edges and of the Fermi Level at the Surface

Let us now examine the distribution of $\emptyset(el/sc)$, the overall potential step, between its components $\emptyset_H$ and $\emptyset_{sc}$. According to the basic laws of electrostatics, the following expression should apply at the phase boundary:

$$\varepsilon_H\mathscr{E}_H = 4\pi Q_{ss} - \varepsilon_{sc}\mathscr{E}_{sc}. \qquad (21)$$

In this equation $\mathscr{E}_H$ and $\mathscr{E}_{sc}$ are the electric field strengths near the interface on the side of the Helmholtz layer and of the semiconductor respectively, ε_H and ε_{sc} are the corresponding static dielectric constants, Q_{ss} is the density of charge on the surface states (depending on ϕ_{sc}), and the minus sign before the second term of Eqn.(21) allows for the inconsistency in the sign convention mentioned above. For approximate calculations we may put $|\mathscr{E}_H| \cong |\phi_H|/L_H$ and $|\mathscr{E}_{sc}| \cong |\phi_{sc}|/L_{sc}$, where L_H and L_{sc} are the thicknesses of the Helmholtz layer and of the semiconductor space charge layer respectively, related to the corresponding capacities by the expressions $C_H = 4\pi\varepsilon_H/L_H$ and $C_{sc} = 4\pi\varepsilon_{sc}/L_{sc}$. If the charge on surface states is small we conclude from Eqn.(21) that $|\phi_H| \ll |\phi_{sc}|$ if the following inequality applies:

$$\varepsilon_{sc}L_H/\varepsilon_H L_{sc} \ll 1 \qquad (22)$$

For reasonable values of the parameters ε_{sc} and ε_H the condition (22) is usually satisfied, since $L_H \ll L_{sc}$. However, in strongly doped semiconductors (in which the concentrations n_0 or p_0 are very high) or at high values of $|\phi_{sc}|$ the thickness L_{sc} may be so small that the inequality (22) fails to apply.

In order to establish the influence of surface states on the potential distribution we must calculate their capacity $C_{ss} = -dQ_{ss}/d\phi_{sc}$. This can be done very simply in the monenergetic model, which assumes that all the electronic energy levels on the surface have the same energy E_{ss}. We can easily show (see, for example, Ref.6) that if

$$N_{ss} > \varepsilon_H kT/(\pi e^2 L_H) \qquad (23)$$

where N_{ss} is the number of surface states per unit surface area of the interface, we must have $|\Delta\phi_H| > \Delta\phi_{sc}|$. In other words, if the condition (23) is satisfied, a change in the potential of the electrode causes a more substantial change in the potential of the Helmholtz layer than in that of the space-charge layer. The critical value of N_{ss} (for which the inequality (22) reduces to an equality) is of the order of 10^{13}–10^{14} cm^{-2}.

Thus, since in most cases $L_H < L_{sc}$, we also have $|\phi_{sc}| \gg |\phi_H|$, and therefore the parameter ϕ_{sc} in reasonably concentrated solutions of electrolytes probably accounts for the greater part of the potential step at the interface [ϕ(el/sc)]. However, this conclusion does not apply in the following cases:

1) when the electrode is strongly charged, and the Fermi level at the surface is brought close to the edge of the appropriate band ("metallisation" of the surface);

2) at high concentrations of surface states, when a change in occupancy (i.e. in the charging) of the surface states causes a marked redistribution of the potential and can significantly increase the contribution of the component ϕ_H at a fixed value of ϕ(el/sc);

3) in heavily doped semiconductors, when the Fermi level in the bulk of the material is close to the edge of the band of current carriers (or even lies within that band, as it does in metals).

All we have said so far applies equally to the distribution of potential at the interface under equilibrium conditions and with polarisation applied to the electrode from an external source of current.

Let us consider the two most important special cases[28–30].

1. Assume that when the electrode potential is changed $|\Delta\phi_{sc}| \gg |\Delta\phi_H|$. This condition means that the potential jump in the Helmholtz layer is practically unaffected by the polarisation of the electrode ($\Delta\phi = -\Delta\phi_{sc}$). Therefore the energy levels on the surface (and, in particular, those of the band edges $E_{c,s}$ and $E_{v,s}$) remain in a fixed position relative to the energy levels of the solution and of the reference electrode (Figs.4*a* and 4*c*). This situation is described as "clamping" of the band edges at the surface.

The physical explanation of the "clamping" effect is that the parameter ϕ_H is mainly determined by the chemical interactions between the semiconductor and the solution and is not affected by external influences (such as polarisation, or illumination). As a result, the position of the band edges at the surface ($E_{c,s}$ and $E_{v,s}$) are the same for all samples of the given semiconductor material in contact with the given electrolyte solution, whatever the type and magnitude of the conductivity, since the chemical nature of the solid is practically unaffected by the doping. Experimental determinations of $E_{c,s}$ and $E_{v,s}$ for various semiconductors[31] have confirmed this conclusion.

2. Assume, conversely, that the polarisation of the electrode gives $|\Delta\phi_H| \gg |\Delta\phi_{sc}|$, i.e. that the change appears mainly in the potential of the Helmholtz layer. Under these conditions (Fig.4*a* and 4*c*) the energy levels at the surface are shifted relative to the energy levels in solution by an amount $\Delta\phi = \Delta\phi_H$. On the other hand, with respect to the Fermi level in the semiconductor (F) the band edges $E_{c,s}$ and $E_{v,s}$ at the surface keep the same position as before the change in the potential of the electrode, since the parameter ϕ_{sc} is unchanged. In order to stress the difference between this case and the previous case the band edges are said to be "unclamped" from the surface (the same phenomenon is sometimes referred to, less accurately, as "clamping" of the Fermi level with respect to the band edges).

The Fermi level "clamping" effect allows the parameter F to reach the value F_{redox} even in systems with very high positive or negative values of the equilibrium potential, in which the level F_{redox} lies outside the forbidden energy gap of the semiconductor. Thus the "clamping" of the Fermi level on a semiconductor electrode allows the electrochemical reaction to proceed under the conditions (13), which could not be achieved with "clamped" band edges.

In real systems we often observe an intermediate case in which polarisation of the electrode affects both the potential steps ϕ_H and ϕ_{sc}, so that in practice neither the band edges nor the Fermi level are clamped. Some results illustrating the "clamping" effects and a more detailed discussion of their origin are given below (Section IV).

3. Determination of the Flat Band Potential

The flat band potential is one of the most important physicochemical characteristics of the semiconductor electrode. In the electrochemistry of semiconductors this concept has become even more important than the zero-charge potential in the electrochemistry of metallic electrodes. The parameter ϕ_{fb} is used in the quantitative description of the double layer structure and of the kinetics of electrochemical reactions on semiconductor electrodes, especially in the photoelectrochemistry of semiconductors, since photocurrents of reasonable magnitude can flow only if the photo-generated electrons and holes can be efficiently separated in the space-charge region (see p.326). This carrier separation is effective only at electrode potentials more positive (for n-type photoelectrodes) or more negative (for p-type) than the flat band potential of the semiconductor (though this necessary condition for the separation of the photo-carriers is not sufficient to ensure the flow of photocurrent).

The capacity of the space-charge region of the semiconductor (C_{sc}) is related, in the case of the formation of a depletion layer, to the potential step in the space-charge layer

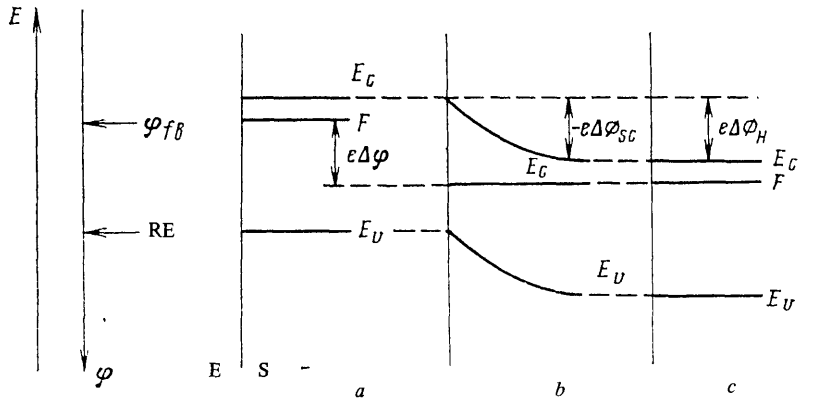


Figure 4. Energy diagram of the interface with an externally applied voltage, showing "clamping" of the band edges (transition from *a* to *b*) and of the Fermi level (transition from *a* to *c*) at the surface of the semiconductor electrode. The initial state *a* is the flat-band case; RE is the reference electrode, E is the electrolyte, S is the semiconductor.

Φ_{sc} by the following expression (written for an *n*-type semiconductor)[1]:

$$C_{sc}^{-2} = \frac{8\pi}{eN_D\varepsilon_{sc}}(|\Phi_{sc}| - kT/e), \qquad (24)$$

According to this equation the plot of C_{sc}^{-2} against Φ_{sc} should be a straight line. Plots in these coordinates are usually called Mott–Schottky graphs (Fig.5). On the assumption that the changes in electrode potential ϕ affect only the component Φ_{sc} and that the capacity C of the contact is equal to C_{sc} we can obtain the concentration of ionised donors from the slope of the straight line, and the flat band potential ϕ_{fb} from its intercept with the potential axis.

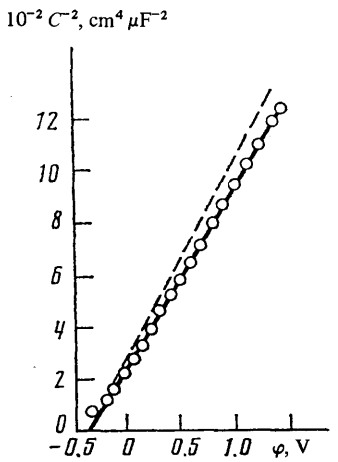


Figure 5. Mott–Schottky plot for a zinc oxide electrode (of conductivity 0.59 Ω^{-1} cm^{-1}) in a 1 *N* KCl solution (pH 8.5).[32] The broken line is calculated by formula (29).

The differential capacity method is widely used in practical electrochemical measurements. We should note, however, that the direct application of formula (24) to the determination of ϕ_{fb} involves a number of assumptions (often not explicitly examined) concerning the properties of the contact between the semiconductor and the electrolyte. The most important of these are:

1. It is assumed that the measured capacity C is not perturbed by the leakage current flowing through the interface, by the finite ohmic resistance of the electrode and of the electrolyte, etc. Accurate corrections for these effects can be calculated (see, for example, Ref.33).

2. It is assumed that the donors (or acceptors) in the semiconductor are fully ionised and uniformly distributed in the space charge region. Deviations from (24) are observed also in the presence of donors (or acceptors) lying deep in the forbidden gap, which are not ionised at room temperature in the bulk of the semiconductor but are partially ionised in the electric field of the space-charge region, thus contributing to the capacity[1].

3. It is assumed that the measured capacity is the capacity of the space-charge region of the semiconductor, and does not include (for example) the capacity of fast surface states, the adsorption capacity, etc. In some cases this condition is satisfied (for example, on the zinc oxide electrode, see below), but often the contribution from the capacity of surface states is substantial.

4. It is assumed that the measured electrode capacity C is unaffected by the Helmholtz layer capacity C_H. Linear plots of the measured capacity C in C^{-2}–ϕ coordinates are usually interpreted (according to formula (24) and to the relationship $C^{-1} = C_H^{-1} + C_{sc}^{-1}$) as evidence that the following conditions are satisfied:

$$C_{sc} \ll C_H, \quad |\Delta\Phi_{sc}| \gg |\Delta\Phi_H|. \qquad (25)$$

However, a detailed study has shown[34] that the possibility of an effect from C_H needs more careful analysis. Thus, if we allow for the change in the potential drop in the Helmholtz layer $\Delta\Phi_H$ caused by the polarisation of the electrode and for the contribution of the capacity C_H to the measured capacity C we obtain [from (24)] the following expression[34] for the

relationship between C and ϕ:

$$C^{-2} = C_H^{-2} + \frac{8\pi}{e\varepsilon_{sc}N_D}(\varphi - \varphi_{fb} - kT/e). \quad (26)$$

We note from (26) that C^{-2} varies linearly with ϕ, i.e. in the same way as C_{sc}^{-2} varies with $\varnothing_{sc}$ (for C_{sc}^{-2} varies with ϕ on the assumption of $\varnothing_H$ = const and $\Delta\phi = -\Delta\varnothing_{sc}$). Furthermore, the slope of the corresponding straight line in $C^{-2}-\phi$ coordinates is the same, according to (26), as the slope of the $C_{sc}^{-2}-\varnothing_{sc}$ straight line (or of the $C_{sc}^{-2}-\phi$ straight line for constant $\varnothing_H$). But in this case the intercept of the straight line with the ϕ axis corresponds, according to (26) to the potential

$$\varphi' = \varphi_{fb} + kT/e - e\varepsilon_{sc}N_D/(8\pi C_H^2). \quad (27)$$

As compared to the potential defined by (24) this potential is shifted by an amount $-e\varepsilon_{sc}N_D/(8\pi C_H^2)$. This shift is far from negligible, especially in heavily doped semiconductors.

Thus the linearity of experimental plots of C^{-2} against ϕ does not necessarily prove that the effect of the Helmholtz layer on the measured value of ϕ_{fb} is negligible, i.e. that the inequalities (25) are satisfied. Conversely, non-linearity of the plot of C^{-2} against ϕ is no proof that the conditions (25) are infringed, i.e. that the Helmholtz layer is responsible for the deviation from linearity.

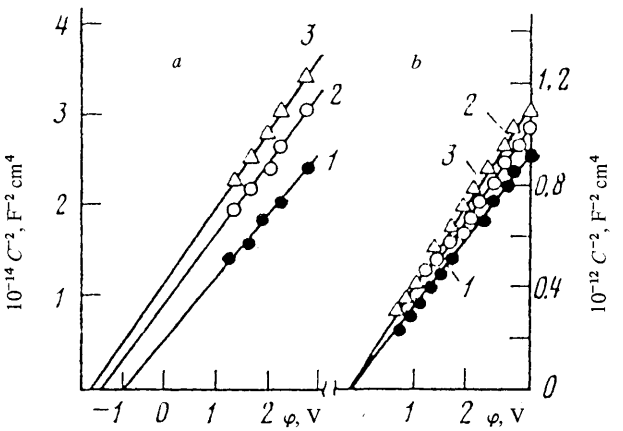


Figure 6. Effect of the frequency of the measuring current on the Mott–Schottky plot[35]: (*a*) CdSe ($N_D = 10^{15}$ cm^{-3}) in a solution of 0.25 M K_2SO_4 + 0.05 M CH_3COOH + 0.05 M CH_3. .COONa, frequency (Hz) 320 (*1*), 2440 (*2*), and 7080 (*3*); (*b*) TiO_2 ($N_D \cong 10^{18}$ cm^{-3}) in a solution of 0.25 M K_2SO_4 + 0.1 M $Na_2B_4O_7$, frequency (Hz) 320 (*1*), 980 (*2*), and 2440 (*3*). Potentials are quoted relative to the normal hydrogen electrode.

Lastly, we should note that ambiguities can arise from the frequency dependence of the Mott–Schottky plots if higher measurement frequencies are adopted in order to minimise the contribution from surface states to the measured capacity. Changes in frequency alter these plots in two ways (see Fig.6). In most cases only the slope changes, and the intercept on the potential axis is unaffected (Fig.6*b*). Sometimes, however, the straight line suffers a shift along the potential axis (as well as a change in slope), and the intercept with the potential axis becomes a function of frequency (Fig.6*a*).

Though a full explanation of these effects has not yet been proposed, plots such as those of Fig.6*b* can be used to measure ϕ_{fb} by extrapolation to the potential axis, though the parameter N_D (or N_A) of course cannot be calculated from the slope. Plots like those of Fig.6*a* are unsuitable even for the determination of ϕ_{fb}.

In addition to the direct experimental determination, a method of calculating the flat band potential ϕ_{fb} from the properties of the semiconductor and those of the solution has been suggested[36].

It follows from (17) and (18) that at thermodynamic equilibrium, and for a high enough concentration of the electrolyte, we can write

$$e(\varnothing_H - \varnothing_{sc}) = F - F_{redox(ref)} = -\chi + F - E_c - F_{redox(ref)} \quad (28)$$

where $(F - E_c) < 0$ is the difference between the F level and the band edge E_c, and $F_{redox(ref)}$ relates to the reference electrode. The electron affinity of the semiconductor χ which appears in Eqn.(28) can be obtained from semi-empirical formulae relating χ to the first ionisation potential I_1 and the electron affinity A_f of the chemical components of the semiconductor, and also the width of the forbidden gap. Thus, in the simplest case of a binary semiconductor MX we have

$$\chi = {}^1/_2(A_f + I_1 + E_g).$$

The difference $F - E_c$ is given by the expression (17), and the quantity $F_{redox(ref)}$ is assumed to be known (see Section II). Lastly, assuming that at the point of zero zeta-potential (i.e. at the iso-electric point) $\varnothing_H = 0$, we can calculate the band bending ($e\varnothing_{sc}$) from (28), and hence arrive at the flat band potential.

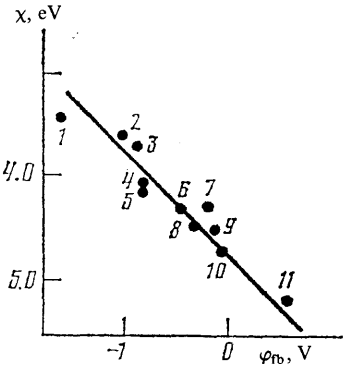


Figure 7. Relationship between the calculated electron affinity and the measured flat band potential (relative to the saturated calomel electrode) for various semiconductors at their isoelectric point[36]: *1*) ZrO_2, *2*) $BaTiO_3$, *3*) $SrTiO_3$, *4*) Ta_2O_5, *5*) ZnO, *6*) TiO_2, *7*) $FeTiO_3$, *8*) SnO_2, *9*) CdO, *10*) Fe_2O_3, *11*) WO_3.

The pH value corresponding to the isoelectric point can be calculated if the standard electrochemical potentials of the reactions involving the adsorbed ions are known, or it can be determined experimentally (as was stated above). This suggests an experimental test of formula (28). In particular, an approximately linear relationship is found between $\varnothing_{sc}$ and

the pH for a large number of oxide semiconductors. An empirical linear relationship between the calculated χ values and the measured ϕ_{fb} has also been reported (see Fig.7). This plot can be used to estimate the flat band potential of any oxide semiconductor for which the parameter χ can be calculated.

To conclude this Section we should note that a linear relationship between χ and ϕ_{fb} is fully analogous to the well known dependence of the electronic work function w on the zero-charge potential in the electrochemistry of metals[25]. The analogy is particularly clear for wide-gap doped semiconductor, for which $E_c - F$ is quite small ($\lesssim$0.1 eV), so that $\chi \cong w$. Under these conditions, as was pointed out in the previous Section, the deviations from the linear relationship found experimentally in some metals can be ascribed to the differences in the dipole potential step created by the adsorption of solvent on different metals[25]. A similar effect can be expected in semiconductor electrochemistry, though of course it cannot be very marked in the case of a series of semiconductor electrodes of similar chemical type.

IV. QUASI-THERMODYNAMIC DESCRIPTION OF PHOTO-ELECTROCHEMICAL PROCESSES

In this Section we shall examine some of the photo-electrochemical phenomena in semiconductor–electrolyte systems under the influence of light. In addition to their intrinsic scientific interest, these phenomena also have a high relevance to the practical exploitation of electrochemical systems involving semiconductor electrodes. The strongest effects on the electrode processes are obtained by using light of frequency higher than the intrinsic (fundamental) absorption threshold of the semiconductor, so that the energy of the light quanta is sufficient to generate electron–hole pairs. The redistribution of the charge carriers in the semiconductor near the solution boundary caused by the photo-generation can drastically affect not only the rate but also the nature of the electrochemical processes in progress.

1. The Quasi-Fermi Level

Several different methods of describing photo-electrochemical processes have been proposed. For example, the kinetics of photo-electrochemical processes have been studied theoretically by solving the transport equations allowing for the photo-generation of carriers, in conjunction with various boundary conditions[37–40]. This approach offers an exact solution of the problem in a number of simple cases, but if the boundary conditions are relatively complex the method becomes laborious and the resulting equations unwieldy. A qualitative understanding, and often a quantitative treatment, can be achieved more simply, on the other hand, by using a quasi-thermodynamic as opposed to a kinetic approach, based on the quasi-Fermi level concept.

It may be helpful to remind the reader of the significance of the quasi-Fermi level[3]. Assume that illumination of the semiconductor leads to additional generation of current carriers. In a stationary regime under these conditions a dynamic equilibrium is established between the generation and the recombination of electron–hole pairs, resulting in the appearance of steady-state (but not equilibrium!) values of the carrier concentrations n_0^* and p_0^*:

$$n_0^* = n_0 + \Delta n, \quad p_0^* = p_0 + \Delta p. \tag{29}$$

Except in the space-charge region $\Delta n = \Delta p$, since the photo-generation process creates pairs of carriers.

By inserting the concentrations n_0^* and p_0^* into (17) we can calculate the position of the "quasi-Fermi" levels F_n and F_p produced by the splitting of the original Fermi level F. Thus, for an n-type semiconductor in which $\Delta n \ll n_0$ we find from (17b) that $F_n \cong F$. At the same time, since $p_0 \ll n_0$, the condition $\Delta p \gtrsim p_0$ may also apply, and therefore the parameter $F - F_p$ according to Eqn.(17b) becomes

$$F - F_p = kT \ln\left(\frac{p_0 + \Delta p}{p_0}\right); \quad F - F_p \simeq kT \ln\frac{\Delta p}{p}, \quad \Delta p \gg p_0. \tag{30}$$

Similar relationships can be written for p-type semiconductors.

Thus according to Eqn.(30) a significant shift in electrochemical potential can be obtained by photo-generation only for the minority carriers.

2. Description of the Main Types of Photo-electrochemical Reaction

Let us now use the concept of the quasi-Fermi level to describe some qualitative aspects of the development of photo-electrochemical reactions at an illuminated semiconductor–electrolyte interface[12,41].

The basic idea underlying our quasi-thermodynamic approach is that the electrode reaction is accelerated by light as a result of the formation of the quasi-levels F_n and F_p, displaced with respect to the equilibrium position of the Fermi level F. We now need to modify the condition (13). The anodic reaction (with the participation of holes) will take place if

$$F_p > F_{redox} \tag{31a}$$

and the cathodic reaction (with the participation of electrons) will take place if

$$F_n > F_{redox}. \tag{31b}$$

Consider first a semiconductor electrode under open-circuit conditions. An example could be a single particle of a suspension of a semiconductor in a conducting liquid. There will be a region of potential for which no electronic transitions take place at the semiconductor–electrolyte interface in the dark, i.e. for which the semiconductor behaves as an ideally polarisable electrode. The upper and the lower limit of this region of potential are the decomposition potential of the solvent and (or) the decomposition (corrosion) potential of the semiconductor. The stationary potential of the electrode in the ideal polarisability region is determined by chemisorption processes (usually, in aqueous solutions, oxygen chemisorption). The same processes also determine the steady-state band bending.

The energy band diagram of a semiconductor (n-type, in this case) in contact with a solution is shown in Fig.8. In addition to the energy levels of the semiconductor (the bottom of the conduction band E_c and the top of the valence band E_v) the diagram gives the electrochemical potential levels for the anodic dissolution of the semiconductor $E_{dec,p}$ and for the cathodic hydrogen evolution E_{H_2/H_2O} (assuming that the most likely anodic reaction is the decomposition of the semiconductor with the participation of holes and the most likely cathodic reaction the evolution of hydrogen from water with the participation of electrons from the conduction band).

The diagram (Fig.8) assumes the formation of a depletion layer in the surface region of the semiconductor. Electrons and holes generated by light in the electric field of the depletion layer move in opposite directions: in the present case

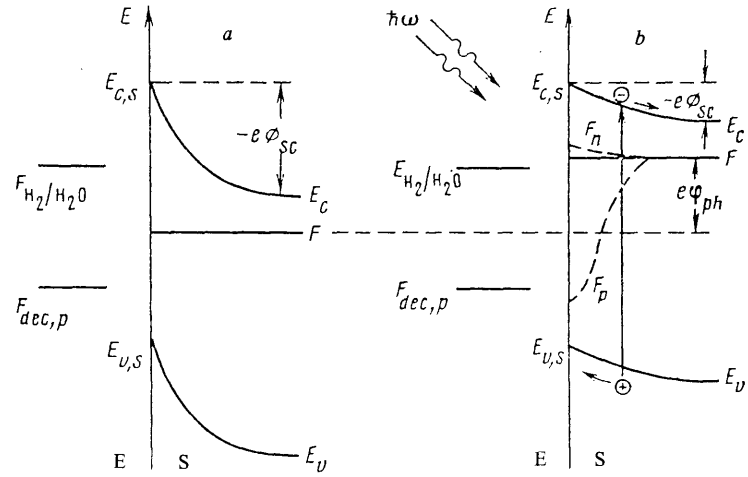


Figure 8. Energy diagram for the contact between a semiconductor and an electrolyte: (*a*) in the dark, (*b*) illuminated; E is the electrolyte, S is the semiconductor.

the holes move towards the interface and the electrons move towards the bulk and away from the interface. The electric field produced by this charge separation partially compensates the field originally present. As a result the bending of the bands ($e\varnothing_{sc}$) decreases, i.e. the bands are flattened.

The flattening of the bands produces, in turn, a change in the mutual configuration of other energy levels in the system. We shall assume, to simplify the problem, that the potential step in the Helmholtz layer is unaffected by illumination ($\varnothing_H$ = const), and hence that the position of the band edges at the surface ($E_{c,s}$ and $E_{v,s}$) is fixed with respect to the reference electrode and therefore also with respect to the energy levels in the solution (band edges "clamped" at the surface, see Section III). At the same time the position of the electrochemical potential F of the semiconductor (Fermi level) is rigidly fixed with respect to the band edges in the bulk of the semiconductor[3]. The result is that under illumination the unbending of the bands "drags" the Fermi level away from the position for the electrode in the dark, as shown in Fig.8. This shift ΔF can be measured by using a reference electrode, and gives rise to the photo-potential $\phi_{ph} = \Delta F/e$.

Consider the effects which accompany the formation of quasi-Fermi levels for electrons and holes. For the majority carriers (electrons) the shift of the level F_n relative to F is very small, as was said above, and can usually be ignored, but for the minority carriers (holes) the quasi-Fermi level F_p can lie relatively far from F in the energy diagram.

At some level of illumination the quasi-Fermi level for holes F_p will reach the level of the anodic reaction on the semiconductor surface (in Fig.8 this is the semiconductor decomposition reaction). Also, because of the shift in the Fermi level F, the quasi-Fermi level for electrons F_n can reach the level of the cathodic reaction (in Fig.8, the evolution of hydrogen from water). The two reactions are induced simultaneously, producing photo-corrosion of the semiconductor. In this way the electrons and holes generated under non-equilibrium conditions in a corrodible semiconductor by illumination are used to accelerate the partial reactions.

In principle the decomposition (dissolution) of the semiconductor could be replaced by another anodic reaction: for example, the oxidation of a dissolved substance or the evolution of hydrogen from water. Obviously, in the latter case the result of the illumination of the semiconductor is the photo-electrolysis of water with formation of hydrogen and oxygen, i.e. the conversion of light (solar) energy into the chemical energy of the products of photo-electrolysis.

When the semiconductor–electrolyte interface is uniformly illuminated the two conjugated reactions proceed at equal rates at each point of the surface. The steady-state potential of the uniformly illuminated semiconductor is a mixed potential. If, on the other hand, the surface of a semiconductor having uniform composition and properties is unevenly illuminated the conditions for the electrochemical reaction are different on the illuminated and on the dark parts of the surface. In this case the conjugated reactions are separated in space, and we can think of local anodes and cathodes. This situation is artificially created, for example, in the selective photo-sensitive etching of semiconductor materials (see below, Section V).

The spatial separation of the anodic and the cathodic reaction on an illuminated semiconductor can be achieved also in other ways: for example, by imparting to specific parts of the semiconductor surface special electrochemical (in particular, electrocatalytic) properties, different from the properties of the rest of the surface. These regions act as local electrodes, and the system as a whole acts as a galvanic couple. An example of this type of micro-heterogeneous system is a suspension of platinised strontium titanate in an aqueous solution. Illumination of this system generates electrons and holes which are separated in the electric field of the depletion layer close to the surface (Fig.9), the holes moving towards the surface of the semiconductor and the electrons towards the bulk, eventually crossing the semiconductor–metal interface into a microscopic inclusion from which they finally enter the solution. In this way hydrogen is generated on the metal surface (in this case, platinum),

and oxygen on the illuminated surface of the strontium titanate. This type of micro-heterogeneous system is currently attracting a great deal of interest for solar energy conversion[42,43].

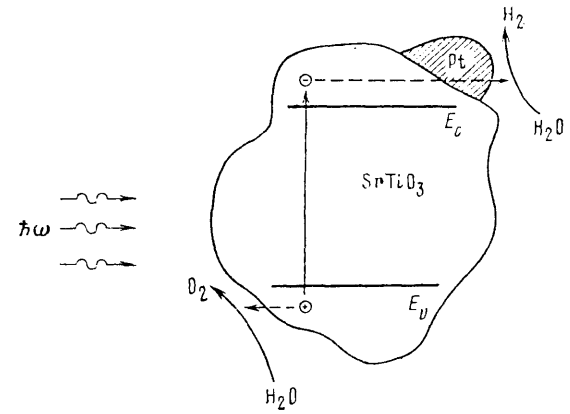


Figure 9. Energy diagram for the photo-electrolysis of water on a particle of a suspension of a semiconductor (platinised $SrTiO_3$) in an aqueous solution.

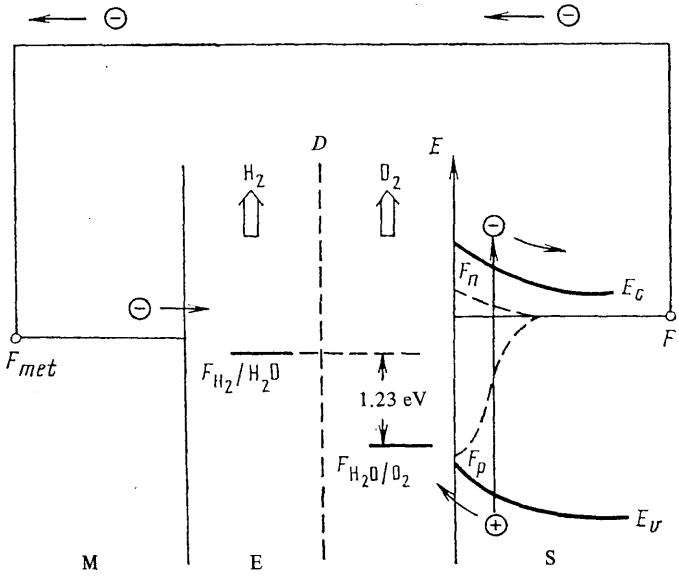


Figure 10. Energy diagram of an illuminated photocell with an *n*-type semiconductor photo-anode for the electrolysis of water: M is the metal, E is the electrolyte, S is the semiconductor, D is the diaphragm.

An obvious development of this approach is to create a macro-heterogeneous system, i.e. a short-circuited electrochemical cell consisting of a semiconductor photo-electrode and a non-photosensitive (e.g., metallic) auxiliary electrode (Fig.10). By making the photo-electrode (as before) of strontium titanate in an aqueous solution we can produce photo-electrolysis of water in the illuminated cell, the products (gaseous hydrogen and oxygen) appearing at the separate electrodes of the cell. The reliable and simple separation of the products of the photo-reaction, which is a direct consequence of the spatial separation of the primary photogenerated current carriers (electrons and holes) under the influence of the field in the space-charge region, is the most important advantage offered by semiconductor photo-electrochemical devices for the conversion of light energy into chemical energy.

The spatial separation of anodic and cathodic partial reactions stimulated by illuminating the semiconductor–electrolyte interface can be useful for two reasons. Firstly, by "leading" the current carriers of different sign to different parts of the surface we can greatly reduce the losses due to recombination and raise the quantum yield of the photocurrent and the efficiency of the conversion of solar into electrical energy. Secondly, the efficiency of the photo-electrolysis can be increased very substantially by transferring one of the two conjugated reactions (the one involving majority carriers) to a separate auxiliary electrode. Thus the cathodic partial reaction (hydrogen evolution, say) can be conveniently carried out on a metallic electrode chosen for its favourable electro-catalytic properties towards this reaction.

Let us now consider a system in which equilibrium is established between the semiconductor and the solution in the dark. This is usually the case when the solution contains an easily reversible oxidation–reduction system. Under these conditions the semiconductor acquires the equilibrium potential of the system, i.e. $\phi = \phi^0_{redox}$, or in other words $F = F_{redox}$.

A similar argument shows that illumination of the semiconductor causes a shift in both the Fermi level F and the quasi-Fermi levels for holes and electrons. Both the forward and the reverse reaction described in Eqn.(1) are accelerated. In other words, the most immediate result of the illumination is an effective increase in the exchange current of the Ox/Red system[44]. This is not the only result, however. If the illuminated semiconductor is an electrode in an electrochemical cell, connected to a counter-electrode through a load resistance, spatial separation of the cathodic and the anodic reaction is obtained as in the photo-decomposition of water discussed above (see Fig.10). The reaction involving minority carriers takes place on the auxiliary electrode. As a result, illumination of the semiconductor electrode induces a current in the external circuit, and in conjunction with the load resistor this produces useful power. In other words, light energy has been converted into electrical energy. This is the operating principle of the photo-electrochemical cell which has been called the "liquid solar cell".

Let us examine in detail the operation of such a photocell taking one specific example (Fig.11): the *n*-type CdS|alkaline solution of S^{2-} and S_2^{2-}| metallic cathode system. In the dark the equilibrium in the cell is

$$S_2^{2-} + 2e^- \rightleftarrows 2S^{2-}, \qquad (32)$$

Both electrodes acquire the equilibrium potential of this oxidation–reduction system, because the Fermi levels of the metal and of the CdS and the level $F_{redox} = F_{S^{2-}/S_2^{2-}}$ in the solution are brought to the same level. Since the equilibrium potential of the oxidation–reduction system is more positive than the flat band potential of the semiconductor ($\phi^0_{redox} > \phi_{fb}$) the surface of the semiconductor becomes depleted, thus allowing the spatial separation of the photogenerated electrons and holes. Illumination of the electrode unbends the bands, shifting the Fermi level F of the semiconductor with respect to its dark value F_{dark} (see Fig.11),

and this produces a change in the potential of the electrode (i.e. it produces a photo-potential ϕ_{ph}).

In the simplest case (which is often met in experiments) the potential step in the Helmholtz layer (Φ_H) is unaffected by illumination, and is also independent of ϕ^0_{redox}. In other words the edges of the energy bands are "clamped" at the surface (see Section III). Under these conditions the maximum value of ϕ_{ph} (corresponding to the open-circuit photo-potential for fully straightened bands) is equal to the initial (dark) potential step in the space-charge layer ($-\Phi_{sc}$), i.e. to the difference $|\phi^0_{redox} - \phi_{fb}|$. Efficient energy conversion is achieved by choosing a combination of semiconductor and oxidation–reduction system in solution for which this difference is as large as possible.

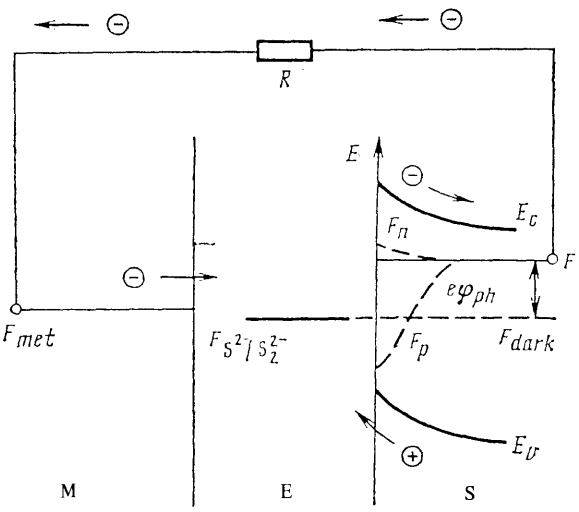


Figure 11. Energy diagram of an illuminated "liquid solar cell" with a CdS photo-anode and an S^{2-}/S_2^{2-} electrolyte; F_{dark} is the Fermi level of the CdS in the dark.

The photo-generation of electron–hole pairs produces quasi-Fermi levels for the minority and the majority carriers, F_p and F_n (see Fig.11). Since on the surface $F_p < F_{S^{2-}/S_2^{2-}}$, and $F_n > F_{S^{2-}/S_2^{2-}}$, both the forward and the reverse reaction are accelerated by illumination in the sulphide–polysulphide system. Closing the circuit through the external load R separates the anodic and the cathodic reaction: the holes flow from the semiconductor photo-anode into the solution, oxidising the S^{2-} ions to S_2^{2-}, and the electrons flow through the external circuit to the metallic counter-electrode (cathode), where they reduce S_2^{2-} to S^{2-}. The potential difference generated across the photo-cell is $I_{ph}R$, where I_{ph} is the photo-current, and the power conversion is $I^2_{ph}R$.

In some cases, however, the potential step in the Helmholtz layer does not stay constant under illumination or after changes in ϕ^0_{redox}. This results in a redistribution of the potential in the double layer, and the photopotential is invariably lower than the difference $|\phi^0_{redox} - \phi_{fb}|$. This occurs, for example, on silicon, gallium arsenide, or molybdenum diselenide electrodes in solutions of various oxidation–reduction systems. In other words, the band edges become "unclamped", and in the limit the Fermi level becomes "clamped" on the semiconductor surface. As a result, a gradual change in the potential ϕ^0 of the oxidation–reduction system causes the open-circuit photo-potential ϕ_{ph} of the cell to increase linearly with ϕ^0 at first ("clamped" band edges), before becoming independent of ϕ^0 ("clamped" Fermi level, see Fig.12).

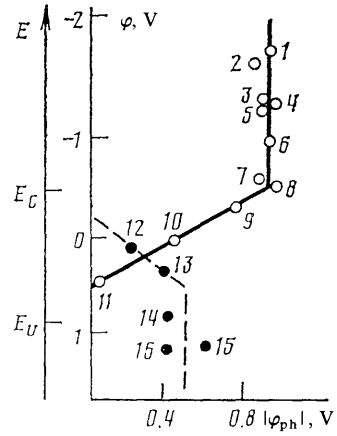


Figure 12. Plot of the absolute value of the open-circuit photo-potential $|\phi_{ph}|$ against the equilibrium potential of the oxidation–reduction system[45]. Photo-electrode of WSe_2, *p*-type (full line) or *n*-type (broken line) in acetonitrile solutions. The oxidation–reduction systems (with charges on the Ox and Red forms shown in brackets) are: *1*) anthracene (0/−1), *2*) phthalonitrile (0/−1), *3*) nitrobenzene (0/−1), *4*) 2,2′-bipyridyl complex of ruthenium (+2/+1), *5*) azobenzene (0/−1), *6*) anthraquinone (0/−1), *7*) benzoquinone (0/−1), *8*) methylviologen (+2/+1), *9*) tetracyanoquinonedimethane (+1/0), *10*) tetramethyl-*p*-phenylenediamine (+1/0), *11*) tetraphenyl-*p*-phenylenediamine (+1/0), *12*) I^-/I_3^-, *13*) Br^-/Br_3^-, *14*) Cl^-/Cl_3^-, *15*) thianthrene (+1/0), *16*) 2,2′-bipyridyl complex of ruthenium (+3/+2). The potentials are quoted against the saturated calomel electrode.

No explanation has yet been put forward for this phenomenon, which seriously limits the application of photo-electrochemical cells to the conversion of solar energy into electrical energy. Possible causes include (see Section III) the strong charging of the semiconductor electrode as the Fermi level approaches the edges of the forbidden gap (for example, during the formation of an inversion layer in the semiconductor[30,46]), a high density of surface states[28,29], or a shift in flat band potential in solutions of oxidation–reduction systems caused by the partial oxidation (or reduction) of the semiconductor surface by the components of this system, making ϕ_{fb} a function of ϕ^0.[47] All these situations could lead to a redistribution of the potential step at the interface between the space charge layer and the Helmholtz layer which could favour the latter layer.

3. Photo-corrosion and Stability

In the field of corrosion and photo-corrosion of semiconductor electrodes the quasi-thermodynamic approach offers useful criteria for determining the propensity of a semiconductor to

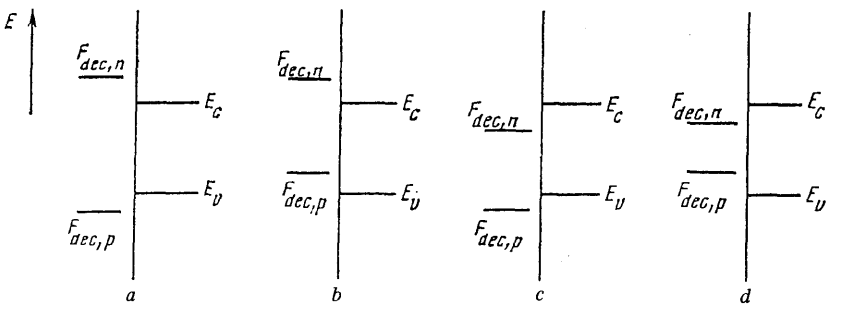


Figure 13. Diagrammatic presentation of the thermodynamic stability of a semiconductor with respect to decomposition in solution: *a*) absolutely stable, *b*) stable towards cathodic decomposition, *c*) stable towards anodic decomposition, *d*) unstable.

photo-corrosion and for identifying means of corrosion protection[12]. For example, in the case of the binary semiconductor MX (where M is the electropositive and X the electronegative component) we can write the following equations for the partial electrochemical reactions: for the cathodic decomposition with the participation of electrons from the conduction band

$$MX + ne^- \rightarrow M + X^{n-} \qquad (33a)$$

and for the anodic decomposition with the participation of holes (h^+)

$$MX + nh^+ \rightarrow M^{n+} + X\,. \qquad (33b)$$

Taking (as a concrete example) the hydrogen electrode as the reference level we can describe the overall reaction in the cell by one of the following equations (with the electrochemical potential of the reaction shown in brackets):

$$MX + \frac{n}{2}H_2 \rightleftarrows M + nH^+ + X^{n-}\,(F_{dec,n})\,, \qquad (34a)$$

$$MX + nH^+ \rightleftarrows M^{n+} + X + \frac{n}{2}H_2\,(F_{dec,p})\,. \qquad (34b)$$

By calculating the free energy change for these reactions we can determine the standard equilibrium potentials for the cathodic ($\phi^0_{dec,n}$) and the anodic ($\phi^0_{dec,p}$) decomposition of the semiconductor.

The thermodynamic condition for an electrode reaction (including a partial corrosion reaction) can be written for the cathodic reaction involving electrons from the conduction band as

$$\varphi < \varphi^0_{dec,n} \quad \text{or} \quad F > F_{dec,n} \qquad (35a)$$

and for the anodic reaction involving holes from the valence band as

$$\varphi > \varphi^0_{dec,p} \quad \text{or} \quad F < F_{dec,p}\,. \qquad (35b)$$

In order to determine the susceptibility of a semiconductor to electrochemical decomposition (or corrosion) in a specific environment we must insert into the energy band diagram the electrochemical potential levels of the electron for reactions (34a) and (34b).

Different possible situations are shown in Fig.13. The semiconductor is stable towards cathodic decomposition if the electrochemical potential level for this reaction lies within the conduction band, and it is stable towards anodic decomposition if the appropriate level lies within the valence band. In both cases if the change in potential takes place entirely within the semiconductor ("clamping" of the bands at the surface) the level becomes "inaccessible" to the Fermi level of the semiconductor. Thus in the situation illustrated in Fig.13*a* the semiconductor is absolutely stable, since the levels of both decomposition reactions lie outside the forbidden gap. More often the semiconductor is found to be stable towards only one type of decomposition reaction: the cathodic (Fig.13*b*) or the anodic (Fig.13*c*). Lastly, when both the $F_{dec,n}$ and the $F_{dec,p}$ level lie within the forbidden gap (Fig.13*d*) the semiconductor can decompose, in principle, under both cathodic and anodic polarisation.

The thermodynamic description of photo-corrosion assumes that the electrode reaction causing decomposition of the semiconductor is accelerated (under the influence of light) by the shift in the quasi-Fermi levels for electrons (F_n) and holes (F_p). We must therefore modify the conditions (35). The cathodic photo-decomposition of the semiconductor involving electrons from the conduction band is subject to the necessary condition [see (31)]

$$F_n > F_{dec,n} \qquad (36a)$$

and the anodic photo-decomposition involving holes to the condition

$$F_p > F_{dec,p}\,. \qquad (36b)$$

As soon as either of the conditions (36) is satisfied the corresponding reaction becomes thermodynamically possible.

We should note that the reaction may nevertheless be kinetically hindered. Thus in many cases it is kinetic rather than thermodynamic features of the electrode reaction which determine the corrosion (or photo-corrosion) behaviour of semiconductor electrodes.

In order to identify means of protection against corrosion (or photo-corrosion) we must consider what other reactions can compete with the photo-decomposition process. For example, at the highest levels of illumination the cathodic reaction with the most positive equilibrium potential is the most probable, and the predominant anodic reaction is the one with the most negative equilibrium potential. It follows that the photo-corrosion process can be suppressed by adding suitable oxidisers or reducers to the solution.

Thus anodic photo-corrosion can be prevented by systems whose oxidation–reduction potential is more negative than the decomposition potential: $\phi^0_{redox} < \phi^0_{dec,p}$, i.e. $F_{redox} > F_{dec,p}$ (see Fig.14). The condition for stabilisation towards cathodic photo-decomposition is $\phi^0_{redox} > \phi^0_{dec,n}$, or $F_{redox} < F_{dec,n}$. These protection systems, which stabilise the semiconductor by being thermselves oxidised or reduced,

are used in photo-electrochemical solar energy conversion cells[48-51]. The solvent (for example, water) can act as the protection additive if it is oxidised (or reduced) more readily than the material of the semiconductor electrode. This occurs, for example, in many oxide electrodes (TiO_2, $SrTiO_3$, etc.), for which the most probable anodic photo-reaction is the oxidation of water to oxygen.

Let us examine from this point of view the photo-corrosion behaviour of GaAs and GaP in aqueous solutions. The electrochemical potential levels for the decomposition reactions of these materials are indicated in Fig.15 in relation to the levels E_C and E_V,

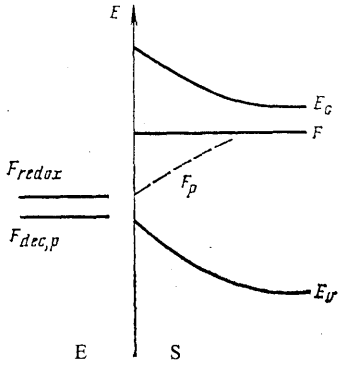


Figure 14. Protection of an n-type semiconductor from anodic photo-decomposition by the addition of an oxidation–reduction system to the solution.

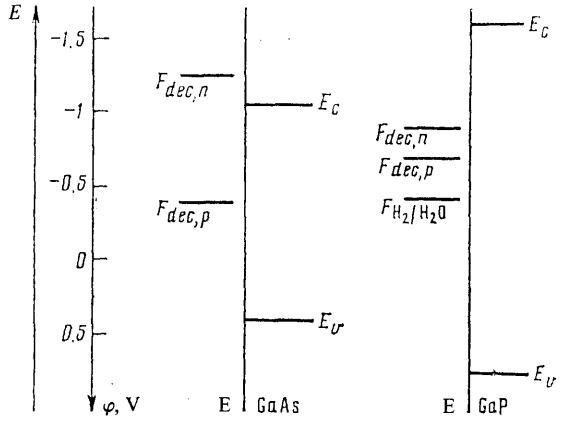


Figure 15. Energy levels at the contact between GaAs or GaP and an aqueous solution at pH 7.[52] The potentials are quoted against the normal hydrogen electrode.

For GaAs the level $F_{dec,n}$ corresponds to the reaction

$$GaAs + 3H^+ + 3e^- \rightleftarrows Ga + AsH_3$$

and $F_{dec,p}$ to the reaction

$$GaAs + 5H_2O + 6h^+ \rightleftarrows Ga(OH)_3 + HAsO_2 + 6H^+.$$

For GaP the level $F_{dec,n}$ corresponds to the reaction

$$GaP + 3H^+ + 3e^- \rightleftarrows Ga + PH_3$$

and $F_{dec,p}$ to the reaction

$$GaP + 6H_2O + 6h^+ \rightleftarrows Ga(OH)_3 + H_3PO_3 + 6H^+.$$

By comparing these diagrams with Fig.13 we note that GaAs is an example of case 13*b*, i.e. it is stable towards cathodic decomposition but potentially unstable towards anodic decomposition, whereas GaP is potentially liable to both cathodic and anodic decomposition, since the levels of both reactions lie within its energy gap (as in Fig.13*d*).

4. Limitations of the Quasi-Fermi Level Concept in Photoelectrochemical Kinetics. Alternative Approaches

As we have shown the quasi-thermodynamic approach based on the concept of quasi-Fermi levels is widely used and, on the whole, effective. It has the undeniable advantages of being physically meaningful and simple. However, it should not be forgotten that the use of the quasi-Fermi level concept is not always justified.

The definition of the quasi-Fermi level within a semiconductor is meaningless unless the following conditions are satisfied:

$$\tau_c, \tau_v < \tau_{cv} \qquad (37)$$

where τ_C and τ_V are the times for the establishment of thermodynamic equilibrium in the electron ensemble of the conduction band and in the hole ensemble of the valence band, and τ_{CV} is the time for the establishment of equilibrium between the electron and the hole ensembles.

The conditions (37) are usually obeyed, but there are additional conditions to be met before this approach can legitimately be applied to the description of electron transfer processes at interfaces. We need to define the times ($\tau_{n,s}$ and $\tau_{p,s}$) elapsed between the photo-excitation of an electron or hole and its capture by the surface (for example, as a result of the electrode reaction). The quasi-Fermi level concept is valid only if these times are greater than τ_C and τ_V, because if the opposite were true insufficient time would be available for the establishment of quasi-equilibrium in the bands, and the "hot" particles would take part directly in the electrode process. On the other hand, the times $\tau_{n,s}$ and $\tau_{p,s}$ must be less than τ_{CV}, because otherwise the electron–hole system would reach full equilibrium and we would revert to $F_n = F_p = F$ close to the surface.

Thus, in addition to (37), the following systems of inequalities must be satisfield:

$$\tau_c < \tau_{n,s} < \tau_{cv}, \quad \tau_v < \tau_{p,s} < \tau_{cv}. \qquad (38)$$

If only one type of carrier is involved in the reaction, only one of these two systems of inequalities has to apply.

If the capture of electrons or holes by the surface is fast, the parameters $\tau_{n,s}$ and $\tau_{p,s}$ are identical to the times of arrival at the interface. If, on the other hand, the surface process cannot be treated as infinitely fast, the times $\tau_{n,s}$ and $\tau_{p,s}$ can be identified with the characteristic times of the process (for example, the time for the elementary act of the electrode reaction). Since the difference between the times τ_C and τ_V (on the one hand) and the time τ_{CV} is fairly large ($\approx 10^{-13}$–10^{-8} s) the conditions (38) are often satisfied, and this explains the success of the quasi-Fermi level concept when applied to various types of heterogeneous process.

Nevertheless, for a quantitative description (see, for example, Ref.53) still further conditions have to be satisfied. In particular, the quasi-levels in the space-charge regions must be reasonably smooth, and the amount of recombination within the space-charge region must be small. Clearly, also, if the carriers are photo-generated near a surface at which a fast electrode reaction is taking place they could be "sucked out" of the semiconductor before coming to equilibrium with the thermalised carriers in the appropriate band. Under these conditions the carrier cannot be described in terms of the quasi-Fermi levels F_n and F_p: it would be more correct to treat the transitions of the carriers from the electrode into the solution not as a quasi-equilibrium but as a dynamic situation, i.e. as separate events[54-56].

The choice between the two approaches to the description of photo-electrochemical reactions (quasi-thermodynamic, or dynamic) in any particular system can be based, in principle, on experimental data[55]. However, the necessary data are scarce and unreliable at present, and this remains a problem for the future.

V. SOME NEW PRACTICAL APPLICATIONS OF SEMICONDUCTOR ELECTRODES

1. Photo-electrochemical Solar Energy Conversion

The photosensitivity of semiconductor electrodes makes the semiconductor–electrolyte interface a potential energy converter for light[57]. A brief description of the mechanism by which photocurrent is induced in a semiconductor electrode was given above (Section IV) for the two most important cases: in the presence of a highly reversible oxidation–reduction system in solution and without such a system (i.e. under conditions which suppress the electrochemical reaction in the dark). In the first case the light energy is converted into electrical energy, in the second into chemical energy. The photo-electrochemical cells corresponding to these two cases are called "liquid solar cells" (or photo-electrochemical cells of the regenerative type) and photo-electrolysis cells respectively. Among the most important photo-electrolysis reactions is the decomposition of water, a possible source of hydrogen as a fuel or as a raw material.

The main advantage of photo-electrochemical cells with semiconductor electrodes (as compared, say, with solid-state semiconductor solar cells) is their relative insensitivity to the crystal lattice perfection and the purity of the semiconductor. Polycrystalline semiconductor electrodes in electrochemical "solar cells" give very effective energy conversion, both in absolute terms and in comparison to monocrystalline electrodes. This offers, at least in principle, the possibility of developing cheap and simple solar energy converters.

The detailed mechanism of the operation of photo-electrochemical converters and the characteristics of specific systems have been discussed in several recent reviews[6,41,48-51,55,58-60], and lie outside the scope of this review. However, it is important at this stage to examine the main problems still to be solved before photo-electrochemical cells can find extensive practical applications.

The main obstacle to the development of "liquid solar batteries" is the photo-corrosion of the semiconductor electrodes, which seriously limits their useful life. In order to eliminate anodic photo-corrosion, for example, a reversible oxidation–reduction system is added to the solution, so that the oxidation of the Red component (a "consumer" of photo-generated holes) competes with the photo-decomposition of the electrode material (see Section IV). In this way it has been possible to eliminate photo-corrosion almost completely in many types of photocell, and to increase the period of continuous operation of the photocell to almost one year. Nevertheless there are other, less obvious mechanisms of degradation of the electrodes[51,61] which prevent photo-electrochemical cells from competing with the useful service life of solid-state solar cells (up to 20 years).

A very real problem in photo-electrolysis is to make the energetics of the electrochemical reaction compatible with the spectrum of solar radiation. The energy distribution of the photons in the solar spectrum is such that the optimum threshold energy of the quantum process chosen for the conversion of the solar energy (i.e. of the semiconductor electrode reaction) lies in the range 1.1–1.4 eV. The free energy for the decomposition of water into hydrogen and oxygen is 1.23 eV, i.e. it lies within the calculated range. However, in practice the reaction requires a large overvoltage. Allowing also for other unavoidable losses, the quantum energy needed for the photo-electrochemical decomposition of water becomes ~2 eV,[58,60] i.e. it is much higher than even the upper limit of the calculated optimum energy range. In other words, in the solar spectrum only a small fraction of very energetic quanta is used directly in the photo-electrolysis of water. (Note that this is far from accidental: indeed, were it not for this condition the relative stability towards solar radiation of a wide variety of living or inanimate systems in nature could not be explained.) This obstacle can be overcome, in principle, in several ways.

1. Carry out the reaction in the photo-stimulated electrolysis regime. In this case the main bulk of the quanta in the solar radiation (of energy in the range 1.1–1.4 eV) is used to excite the photo-electrochemical reaction, and additional energy (to the required 2 eV) is provided from an auxiliary source. The most successful use of this procedure is reported in Ref.62.

2. Carry out a process of the "two-quantum" type. By combining within the same photo-electrochemical cell two semiconductor photo-electrodes (an n-type anode and a p-type cathode) we can achieve effective addition of the photopotentials developed on the two electrodes (if their characteristics are suitably chosen) and thus obtain the energy needed for the photo-electrolysis of water[63].

Another approach is to carry out the water decomposition reaction in two separate steps, each in a separate photo-electrochemical cell. The two cells are connected by an intermediate substance which acts as a charge transfer medium and is not consumed by the reaction, but ensures that the chemical potentials developed in the two cells are "connected in series"[6,64]. The analogy between this system and the combination of two photo-systems in natural photosynthesis processes is easy to see.

All these approaches rely on the use of two photo-electrodes, and therefore the overall reaction is formally a two-quantum process, which makes possible the required energy gain.

3. Separate the overall process into two steps: the conversion of the solar energy into electrical energy and the electrolysis of water[65-67]. The single photo-electrochemical cell is replaced by a combination of a solar cell (of the solid-state or of the "liquid" type) and an ordinary electrolysis cell. In this case the two functions (development of an electrical voltage and electrochemical decomposition of water) which were combined in the photo-electrolysis cell are now separately assigned to two specially designed pieces of apparatus. In this way we can generate the required voltage by connecting in series several solar cells; greater flexibility in the choice of the photoelectric and electrocatalytic properties of the electrode materials is also possible.

4. Dehydrogenation of cheap and readily available substances. Since the only wanted product is hydrogen, we can abandon the photo-electrolysis of water and choose an alternative electrochemical reaction with a smaller free energy change: for example, the dehydrogenation of various industrial by-products. Photo-electrochemical processes of this type have been studied intensively in recent years[50,68-71].

Other systems of interest include the use of the invisible (infrared) part of the solar spectrum in addition to visible light[72], and the exploitation of non-traditional reactions such as photo-intercalation into the semiconductor crystal lattice of atoms produced by the electrode reaction[73].

The extensive work currently in progess in this area should result in the development of simple and economically attractive photo-electrochemical processes able to compete with other, non-electrochemical methods of utilising the sun's energy.

2. Laser Etching of Semiconductors

Recent advances in quantum optics have led to the development of a new technology: the laser electrochemistry of semiconductors[74,75]. This field includes several topics related to the stimulation of electrochemical processes on semiconductor electrodes by laser radiation. The most successful of these so far has been the photo-sensitive etching of semiconductors with coherent laser radiation for optical information storage (for example, in holography[76]). Light-sensitive etching in conjunction with polarisation from an external source is called photo-anodic etching, whereas etching in an oxidising solution is called photochemical.

The basis of light-sensitive etching is the influence of illumination on the concentration of minority carriers, which determines the rate of dissolution and corrosion processes in semiconductors.

In laser etching an initially flat semiconductor surface immersed in a solution of electrolyte is exposed (through the solution) to two coherent monochromatic beams of light, incident at equal angles, lying in the same plane, and having the same intensity and wavelength. The interference between these beams produces bands of light and dark regions, and stimulates non-uniform etching of the surface.

The theory of laser etching[74,77] can be used to calculate in simple but practically important cases the characteristics of the etched outline as a function of the parameters of the radiation, of the properties of the semiconductor, and of the special features of the electrode reaction. The profile of the etched pattern is very close to sinusoidal. For the case of "surface-absorbed" light (i.e. light with a very high absorption coefficient) and a fast electrochemical reaction the repetition frequency of the profile (having the dimensions of reciprocal length, d^{-1}) is found to be very high. The physical meaning of this observation is the following: if the holes are generated immediately below the surface, and used in the reaction effectively in the same place, we can ignore the diffusion of photo-generated holes beyond the illuminated regions of the semiconductor.

Thus the spatial resolution of light-sensitive etching, i.e. the maximum achievable value of d^{-1}, is not determined by the diffusion length L_p of the holes, as could have been expected ($d \cong L_p$), but it can have a much higher value ($d^{-1} \gg L_p^{-1}$).

It is now experimentally established that the resolving power of the photo-electrochemical information storage processes d_{max}^{-1} (the maximum number of lines etched in the grating per 1 mm) can be very high: for GaAs and CdS it is greater than 6000 mm^{-1}. We should stress that in materials with a high diffusion length L_p (like silicon and germanium) the resolving power is appreciably higher, as could have been predicted theoretically from the L_p values.

In conclusion we note that the laser electrochemistry of semiconductors is not confined to light-sensitive etching. It includes, for example, the study of threshold electrochemical reactions stimulated by powerful laser pulses. These reactions can occur by new paths, yielding new products, owing to the participation of strongly excited species from the solution and of the non-equilibrium electron–hole plasma of the semiconductor. Therefore they offer new possibilities for the development of unconventional processes in chemical technology.

3. The Ion-selective Field-effect Transistor

The combination in a single device of an ion-selective electrode and a field-effect transitor has yielded a new type of detector of ion concentrations called the ion-selective field-effect transistor. Because of its high sensitivity and selectivity coupled with a small size this device has found wide applications in industry, in medicine and biology, and in scientific research.

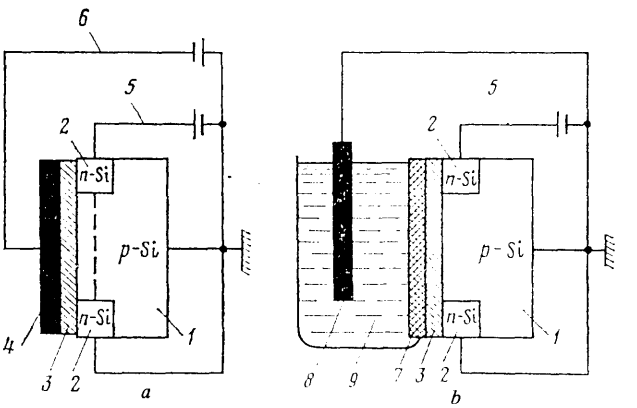


Figure 16. Electrical circuit of a field-effect transistor (*a*) and of an ion-selective field-effect transistor (*b*): *1*) base, *2*) source and drain, *3*) dielectric layer, *4*) gate, *5*) and *6*) low-impedance and high-impedance electric circuits, *7*) ion-selective membrane, *8*) reference electrode, *9*) experimental solution of electrolyte.

The operating principle of the field-effect transistor can be briefly described as follows (see, for example, Ref.78). The transistor (Fig.16*a*) is a metal–dielectric–semiconductor system, i.e. it consists of a semiconductor base on which a dielectric layer and a metallic electrode (the "gate") are deposited. The base is usually a plate of *p*-type silicon, and the dielectric a layer of SiO_2 or Si_3N_4 100–200 nm thick and having a resistance of ~10^{13} Ω. Two regions in which the conductivity type of the silicon is inverted are prepared in the base by localised doping: these *n*-type regions are called the "source" and the "drain" respectively. By inserting voltage sources into the gate–base and source–drain circuits (Fig.16*a*) we can induce a field effect in the transistor. In the absence of a gate voltage the current in the

source–drain circuit is almost zero, because one of the two p–n junctions in this circuit is always reverse-biassed. We now apply to the gate a voltage of sign and magnitude such that an inversion layer is formed near the silicon–dielectric interface (i.e. a layer in which the concentration of minority carriers is greatly increased). In the case shown in Fig.16*a* the gate bias has to be positive with respect to the base. The resulting n-type "channel" short-circuits the source and the drain, allowing current to flow in this circuit (whose resistance is now of the order of 10 Ω). Thus a change in voltage in the high-impedance gate–base circuit effectively controls the current in the low-impedance source–drain circuit, i.e. the device offers a high current gain.

This property of the field-effect transitor is exploited in the ion-selective field-effect transitor to achieve a high sensitivity. The dielectric layer is replaced by an ion-selective membrane, permeable to one kind of ion#, and the metallic gate is replaced by a solution of electrolyte in which the reference electrode needed to complete the electrical circuit is immersed (Fig.16*b*). The role of the external gate voltage is now played by the potential generated on the membrane by the presence of ions to which the membrane is selectively permeable. The magnitude of this potential is given by the Nernst equation [see also formula (4)]

$$\varphi = \varphi^0 + RT/z\mathcal{F} \ln a \qquad (39)$$

where a and z are the activity (in the simplest case, the concentration) and the charge of the potential-determining ion, and ϕ^0 is the standard potential (i.e. the value of ϕ when a = 1 mole litre^{-1}).

For a membrane potential produced in this way the current in the measuring circuit is a function of the activity of the ions (a), thus making the ion-selective field-effect transistor a very sensitive ion detector. A great variety of specific types of this device has been produced, covering a wide range of membrane composition, type of reference electrode, operating regime (for example, including a small auxiliary polarising voltage), etc. A list of the most important of these systems, with a statement of their characteristics and of their application regions, can be found in recent review articles[79,80].

VI. CONCLUSIONS

We have not been able to include in this review all the new ideas and approaches now being actively developed in the field of semiconductor electrochemistry. In conclusion, therefore, we shall simply list the directions which we believe to be the most interesting and promising, though in some cases (for various reasons) interest has only been transient and developments only preliminary. A special discussion of these topics is given in Heller's monograph[61].

New systems. Among the most interesting new materials for practical applications in electrochemistry are the semiconductors with a layer crystal structure[81]. Being d-semiconductors they could be more stable towards photo-corrosion than the semiconductors (mainly sp) discussed above; furthermore, semiconductors with a layer crystal structure can be used as hosts to non-tranditional types of photo-electrochemical reaction: for example, the photo-intercalation of atoms from the solution into the crystal lattice of the semiconductor electrode. Semiconductors with d bands are potentially suitable as electrodes in photo-electrochemical cells. The synthesis and study of new materials with a prescribed set of photo-electric and electrochemical properties have grown into a major activity in the "electrochemical materials science" of semiconductor technology (see, for example, Ref.82).

Another promising area is the study of the photo-electrochemical properties of micro-heterogeneous semiconductor systems: porous electrodes, and suspensions of different particle size (down to colloidal dimensions), in which the photosensitivity of semiconductors is combined with the high catalytic activity of systems having a developed surface.

The modification of semiconductor electrode surfaces by "attached" catalysts (charge carriers)[83] is also being intensively studied at present.

New methods of investigation. Important new information can be expected to flow from the new methods of investigation, both those developed independently within the electrochemistry of semiconductors and of metals and those imported from other disciplines (mainly from surface physics), which have been called non-traditional. The latter relate almost invariably to the effect of radiation on a phase boundary. They include photo-temperature spectroscopy, in which the part of the absorbed light energy used in the photo-electrochemical reaction and that dissipated as heat are distinguished by monitoring the temperature of the photo-electrode, thus allowing the "true" quantum yield to be calculated[84,85], high-time-resolution measurements of the photocurrents induced by nanosecond laser pulses[86,87], electro-luminescence studies of recombination processes in electrodes[88], the photo-emission of electrons from semiconductors into solutions of electrolytes[20], and also the electro-reflectance of light at the semiconductor–electrolyte interface[89]. Photo-acoustic spectroscopy also has been used to study the fine details of the absorption of light by semiconductors[90].

Thus the recent advances have given a fairly comprehensive formulation of the electrochemical behaviour of semiconductors. Because of the number and importance of the new problems, semiconductor electrochemistry has become one of the "growth areas" of modern science.

#In some types of device the membrane is placed directly over the dielectric layer, giving a "four-layer" system.

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Oxidative Dissolution of Transition Metals in a Liquid Phase. Role of Oxygen and of the Surface Oxide Layer

I.P.Lavrent'ev and M.L.Khidekel'

The results of recent studies of the oxidative dissolution of transition metals in a liquid phase are generalised, and an analysis of the role of molecular oxygen and of the oxide film on the metal surface in oxidation processes in donor-acceptor organic media is proposed. The prospects of oxidative dissolution as a direct (single-stage) method of preparation of transition metal complexes are examined. 115 references.

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I. INTRODUCTION

The oxidative dissolution of transition metals in the liquid phase takes place by the reaction

$$M^0 + Ox \xrightarrow[-ne]{mL} L_mM^{n+} + Red + P \qquad (1)$$

where M is the metal, Ox is the oxidiser, L is the complex former, Red is the reduced form of the oxidiser, and P are the products of the interaction between the components of the medium. Oxidative dissolution is an important topic in chemistry and in the chemical industry. It includes problems in catalysis, corrosion, and refining, in the analysis of metals and alloys, in extraction, and in the synthesis of complexes of various types[1]. Many problems in chemical energetics, ecology, and space technology are ultimately determined by metal oxidation processes.

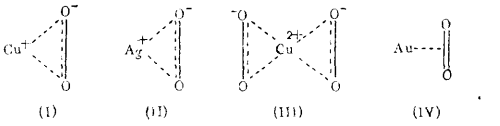
Aqueous media containing inorganic acids, peroxides, and various related composition[2-6] are often used at present for oxidative dissolution. These systems are not always compatible with modern technology, and have some serious limitations (inadequate selectivity, reliance on toxic reagents, etc.). Requirements for non-aggressive and selective processes for the oxidation of metals in the liquid phase are increasing. One promising approach to the development of processes having the required characteristics is the use of non-aqueous media. Unlike the traditional processes in aqueous media, these have not so far been studied in detail.

Interesting influences of dipolar compounds having donor–acceptor properties on the rate and on the direction of chemical reactions have recently been reported: the effects are due to complex formation with organic or inorganic components[7,8]. The use of non-aqueous media allows the choice of a very wide range of donor–acceptor systems and can therefore lead to the development of processes for oxidative dissolution under mild conditions[9].

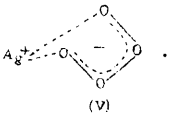
Whether a thermodynamically allowed oxidative metal dissolution process in a liquid phase can be realised, and the rate of the process in practice, are determined by a combination of factors: the nature of the metal and of the oxidiser, the composition of the medium and its donor–acceptor properties, and the state of the metal surface[10]. A real metal surface adsorbs mainly oxygen and water vapour[11]. Therefore an important feature of the process is that it takes place on the surface of an oxide layer. In this review we shall examine the problems arising from the influence of the surface oxide film and of the molecular oxygen on the oxidative dissolution of transition metals in donor–acceptor media, and we shall demonstrate the possibility of the single-stage preparation of transition metal complexes.

II. GAS-PHASE INTERACTION OF MOLECULAR OXYGEN WITH METALS

In order to characterise the interaction between molecular oxygen and a metal surface in a liquid phase, and the type of compound produced by this interaction, we must consider the reaction between metals and oxygen in the gas phase. The atoms of transition metals such as Ni, Cr, Cu, Ag, Au, Pd, Pt, Rh form complexes of the following types with molecular oxygen[12-14]:



Whereas a superoxide anion radical is produced by the interaction of O_2 with Ag and Cu [complexes (I)–(III)], the bond between the oxygen molecule and gold is of the "olefin" type, i.e. the resulting complex (IV) is of the π rather than of the σ type. The possibility of stabilising the bivalent state of the metal leads to the formation not only of $M^+O_2^{\cdot}$ [(I) and (II)] but also of *bis*(dioxygen) complexes such as $Cu^{2+}(O_2^{\cdot})_2$ (III), $Pd^{2+}(O_2^{\cdot})_2$, or in the case of silver (for which this possibility does not exist) we could have the tetra-oxygen complex $Ag^+(O_4^{\cdot})$ (V):



(V)

The formation of complexes of the type of (V) on a metal surface is unlikely for steric reasons. It has been suggested that $AgO_4^{\pm}$ or Ag_2O^{2-} can be formed on a silver surface [i.e. on $Ag(O_2)(ads)$] as a result of the dissociation of the O=O bond[15].

III. LIQUID-PHASE INTERACTION OF MOLECULAR OXYGEN WITH A METAL SURFACE

We have discussed[16] the role of the oxide film on the surface and that of molecular oxygen in the oxidative dissolution of transition metals. Donor–acceptor oxidising systems of two types were studied:

$$\text{DMSO} + \text{RX} \qquad (2)$$

where R = alkyl, H, or CCl_3, and X = Cl, Br, and

$$\text{DMFA} + CCl_4 \qquad (3)$$

In these expressions DMSO is dimethylsulphoxide, and DMFA is dimethylformamide. The system (2), unlike (3), can donate oxygen and thus produce an oxide film on the metal surface:

$$(CH_3)_2SO \rightarrow [O] + (CH_3)_2S.$$

Thus we know that the lower-valency complexes of titanium, molybdenum, and tungsten are effective deoxygenating agents because of the high thermodynamic stability of the M=O bond, and they can reduce $(CH_3)_2SO$ to $(CH_3)_2S$.[17]

We also showed[16] that the metals (M) can be classified into two groups according to their behaviour towards oxidation.

1. Metals which go into solution as complexes of the ionic $[L_pMX_n]_q[MX_m]$ or the neutral type $[L_pMX_m]$. No oxygen is included in these complexes. For the metals in this group, i.e. (Ti), Cr, Mn, Fe, Co, Ni, Cu, (Mo), Rh, Pd, Ag, Cd, (Ir), Pt, and Au, the dissociation energy of the metal–oxygen bond is $E_{MO} < 480$ kJ mole^{-1}.[18] For metals of the first transition series, and also Mo and Re, the rate of oxidative dissolution and the sublimation energy vary in opposite senses.

2. Metals for which the dissociation energy of the M=O bond is $E_{MO} > 480$ kJ mole^{-1} either do not dissolve or go into solution as oxo compounds of the type of $(L_pMO_nX_m)$. This group includes (Ti), V, Zr, Nb, Ru, Hf, Ta, W, (Mo), Re, Os, and (Ir). It was pointed out[18] that the heat of atomisation of O_2 ($E_{OO} = 498.7$ kJ mole^{-1}) lies in this energy range (480–500 kJ mole^{-1}), and therefore a stable M=O bond can be formed in the complexes of these metals.

The mechanism of the oxidative dissolution of the transition metals with the participation of oxygen is extremely complex, and not fully understood[8,9,19,20]. As in the mononuclear complexes of the transition metals with an O_2 molecule we can expect either a labile oxygen-containing molecular complex or a peroxo complex to be formed on the surface[21,22].

The presence of electrons on the oxygen π^* orbitals lowers the bond order in the resulting molecular ions $O_2^{\pm}$ and O_2^{2-}. Accordingly, the distance between the oxygen atoms increases in the series $O_2 < O_2^{\pm} < O_2^{2-}$, and the average energy of the bond decreases[22]. On metals with $E_{MO} \geq E_{OO}$ the states including $O_2^{\pm}$ and O_2^{2-} complexes will have a low stability, and the decomposition of molecular oxygen to form an oxide layer on the surface becomes possible.

The rate of dissolution of metals in the first transition series, and also Mo and Re, in systems (2) and (3) is found to be appreciable. Depending on the energy of the metal–oxygen bond formed on the metal surface by the adsorption of an oxygen molecule in the presence of a donor–acceptor system taking part in the formation of a molecular complex (MC)†, the formation of intermediates and of the final complexes can follow different mechanisms. An analysis of the metal–O_2–MC system has shown[26] that the complex can decompose on the surface either with regeneration of molecular oxygen (if $E_{-O_2-MC} < E_{O=O} > E_{MO}$) or with insertion of oxygen into the products. The formation of a stable oxide ($E_{MO} > E_{MX}$) suppresses this process. Thus, depending on the nature of the metal, oxygen can act as a catalyst (for a number of molecular complexes (MC) in the oxidation of Ag, Au, and Hg with $E_{MO} < 250$ kJ mole^{-1}), as a stoichiometric reactant (for most of the transition metals with $E_{MO} \cong 250$–630 kJ mole^{-1}), and lastly as an oxidative dissolution inhibitor (for Ti, Zr, Nb, Hf, Ta, and W, with $E_{MO} > 630$ kJ mole^{-1}).

We note that under real conditions (i.e. in a medium of coordinating solvents with donor–acceptor properties) dissolved oxygen forms reversible molecular complexes (for example, $C_6H_5N(CH_3)_2.O_2$ with dimethylaniline[27] and $(C_2H_5)_3N.O_2$ with triethylamine[28]), or associations (for example, $(H_2O)_n.O_2$ with water[29]). The energy degeneracy of the π^* orbitals of molecular oxygen is lifted in solution, but not enough for the paramagnetic properties to be lost. In the adsorption of solvated oxygen on the metal surface the splitting of the energy levels of the oxygen may be so large that singlet oxygen is formed: under these conditions changes in spin multiplicity become possible as a result of the change in the magnetic state of the metal atom (or ion)[30]. The transition $O_2(^3\Sigma) \rightarrow O_2(^1\Delta)$, requires an energy expenditure of ~96 kJ mole^{-1}.[31] Singlet oxygen acts as an electron donor towards strong electron acceptors[32], so that the energy consumed in the formation of a solvated molecule of singlet oxygen bound as a complex to the metal surface is compensated by the energy evolved by the addition of one electron to form an anion radical ($O_2 + e \rightarrow O_2^{\pm}$; $\Delta H^{\circ}_{298} = 63$–88 kJ mole^{-1}.[18–33]

The solvated superoxide ion can exist in two resonance-stabilised states: $O_2^{\pm}L \leftrightarrow O_2.L^{\pm}$ (for example $O_2^{\pm}Py \leftrightarrow O_2.Py^{\pm}$).[34] On the other hand, as we have already pointed out, the compounds which we are treating as "solvents" can form molecular complexes or associations (MC) or charge transfer complexes (CTC) with electron acceptors, for example $Py.SO_3$, $Py.Br_2$,[35] and $DMSO.SO_2$.[36]

We conclude from these results that the important role of molecular oxygen in metal oxidation processes reflects the ability of oxygen to interact with both the metal surface and the components of a donor–acceptor system.

IV. ROLE OF THE OXIDE FILM ON THE METAL SURFACE IN OXIDATIVE DISSOLUTION IN THE LIQUID PHASE

1. Formation of an Oxide Film

The electronic structure of the *d* metals is characterised by the presence of collectivised and of localised electrons. The properties of atoms on the surface of the transition metals play an important role in processes such as adsorption and catalysis, and thermo-electron emission.

The asymmetry of the attractive and repulsive forces towards neighbouring atoms of the crystal lattice gives the surface atoms a high reactivity, resulting from the tendency for the field of interaction forces to restore its symmetry. This tendency manifests itself in the formation of additional

† The molecular complexes are of the DMSO.RX and DMFA. $.CCl_4$ type. The formation of MC or associations and in some cases of an ion–radical salt (IRS) stimulated by the activated metal surface cannot be excluded[23–25].

bonds between the surface metal atoms and other atoms or molecules present on the surface. Complex formation on the surface lowers the thermodynamic potential of the system, and it is therefore an energetically favourable and spontaneous process. A study[37] by γ-resonance spectroscopy of the state of iron atoms on a polycrystalline tungsten surface has shown the presence of broken chemical bonds on the metal surface. This must lead to the formation of reactive centres at which relatively stable surface complexes (or even stable chemical compounds) can be formed.

Metal surfaces are covered with a thin layer of oxide (or, in the case of silver, of sulphide), approximately 100 Å thick. Though this layer is too thin to disguise the "metallic" sheen of the surface, there can be no doubt of its presence, and therefore all the processes known to occur on a metal surface have to take place on the surface of the corresponding oxides, which have the properties of semiconductors[38,39]. Only the oxides Au_2O_3, AgO, and Ag_2O_3 are thermodynamically unstable under normal conditions. On the surface of the precious metals gases such as oxygen and hydrogen form adsorption layers[40]. In some cases the heat of adsorption of oxygen at temperatures close to normal (i.e. the oxygen affinity) is higher than the heat of formation of the oxide: it has been suggested[41] that the thermodynamic properties of oxide films of thickness equivalent to one or a few unit cells of the crystal lattice are different from those of the massive oxides, and that the properties of chemisorbed oxygen are similar to those of oxygen in the thin oxides. The distinction between "chemisorbed oxygen" and "phase oxygen" is becoming blurred. Data on the heat of formation of oxides (expressed per mole of oxygen) and on the heat of adsorption of oxygen on various transition metals are given in Table 1.

Table 1. Heat of adsorption (ΔH_{ads}) of oxygen and heat of formation (ΔH) of transition metal oxides (kJ mole^{-2} O_2).[43,44]

Oxide	$-\Delta H$	$-\Delta H_{ads}$	Oxide	$-\Delta H$	$-\Delta H_{ads}$
Ag_2O	61.1	226.1	NiO	489.0	231.9—628.0
PdO	170.8	100.5	FeO	533.4	314.0
PtO_2	58.6	111.0	CoO	479.0	502.4
Cu_2O	333.7	343.3—502.4	WO	854.1	628.0—649.0

Benard[42] has classified all metals into four groups according to their oxygen affinity (ΔH°_{298}, kJ mole^{-1}): 1) $\Delta H^\circ_{298} < 210$ (the precious metals), 2) $\Delta H^\circ_{298} = 210$–$550$ (Cu, Fe, Ni, Co, ...), 3) $\Delta H^\circ_{298} = 550$–$840$ (Mn, Cr, Mo, W, ...), 4) $\Delta H^\circ_{298} > 840$ (Ti, Al, Si, ...). Oxides of the metals in the third and fourth of these groups are difficult to reduce.

The most probable configuration of the adsorption layer varies with the type of crystal plane of the metal, depending on the geometry of the lattice and on the number of bonds which can be formed between the metal and the adsorbed molecule. In the limit of the dissociative adsorption of oxygen the position of the adsorption centres is determined by the crystallographic orientation of the surface. On a close-packed surface, for example on the (111) plane of a face-centred cubic metal like Cu, the most stable adsorption centres are directly above the centres of gravity of groups of three adjacent atoms, and not above the atoms themselves[43] (see Fig.1). This important observation shows that coordination interaction can involve several surface atoms (or molecules): in other words, the conditions in this system are conducive to collective interactions.

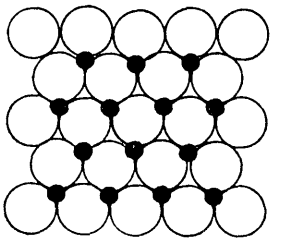


Figure 1. Coordination of the oxygen atoms during the dissociative adsorption of O_2 on the (111) face of a face-centred cubic metal (Cu).[42]

2. Properties of the Oxide Layer

The oxide systems of the transition metals include phases showing substantial deviations from the apparent stoichiometric composition. Typical of these are the homologous series of oxides in which the oxidation number of the metal is not a simple integer[39], for example the titanium oxides[45] Ti_nO_{2n-1} (n = 4–38) and the tungsten oxides[46] W_nO_{3n-2} and vanadium oxides[47] V_nO_{2n-1}, etc., where n is the number of metal atoms in the oxide.

In contrast to the separate amorphous or crystalline oxides, the oxide layers on a metal surface show a number of specific features# when examined as phases in their own right. Near the metal–oxide interface adjacent to the metal surface the oxide has n-type conductivity, i.e. the oxide is non-stoichiometric with an excess of metal. This produces an ohmic contact at the metal–oxide boundary (Table 2), since for most metals the electronic work function is lower than the work function of the oxide. As a result, under thermodynamic equilibrium conditions the oxide layer is enriched with electrons from the metal.

Some of the lower oxide phases of the transition metals, for example TiO,[49] and also the higher oxides of the platinum group metals, for example RuO_2, have a metallic conduction[50]. The possibility and the rate of the oxidation of the metal through the "outer" oxide surface are determined by the difference in work function between the metal and the oxide $\Delta\phi_{OM} = \phi_O - \phi_M$ (where ϕ_M is the electronic work function of the metal and ϕ_O is that of the oxide), and also by the activation energies for conduction (E_C) and for the diffusion of ions (E_d) in the oxide layer.

No direct relationship can be discerned between the $\Delta\phi_{OM}$ values (Table 2) and the ease of oxidation of metals. However, metals for which $\Delta\phi_{OM} \cong 1.0$–$2.5$ eV and the oxide has an energy gap $W \cong 1$–2 eV (like Mn and Cu) are more readily oxidised than metals with a smaller work function difference ($\Delta\phi_{OM} \cong 0$–1 eV) and a forbidden gap $W > 2$ eV (Ti, W). The relative positions of the energy levels of the metals and oxides are shown in Fig.2.

It has been shown[48] that the lower oxide of iron directly adjacent to the metal and structurally bound to it has a different stability (over thicknesses of the order of a few tens of Å units) than the same oxide in isolation from the metal surface.

Table 2. Physicochemical properties of the transition metal and their oxides[18,51-57].

Compound	φ, eV	$\Delta\varphi_{OM}$, eV	$\Delta H^{\circ}_{f,298}$, kJ mole^{-1}	I, eV	Conductivity*	W, eV
Cu	4.55	—	352.1	7.68	met.	—
Cu_2O	5.15	0.60	—	—	p, (n)	1.85
CuO	5.34	0.79	—	—	p, (n)	2.2
Ag	4.49	—	297.7	7.54	met.	—
Ag_2O	—	—	—	—	p	1.57
AgO	—	—	—	—	p	0.7
α-Ag_2S	—	—	—	—	n, (p)	1.34
Au	5.32	—	354.2	9.18	met.	—
Au_2O_3	5.8	0.48	—	—	n	—
Ti	4.05	—	482.3	6.83	met.	—
TiO	3.1	−0.95	—	—	n, (met.)	0
Ti_2O_3	—	—	—	—	p, (met.)	2.2
TiO_2	4.7	0.65	—	—	n	3.1
V	4.28	—	517.1	6.74	met.	—
VO	—	—	—	—	n, (p)	0.2
V_3O_5	—	—	—	—	n, (met.)	—
V_2O_3	—	—	—	—	n, (met.)	0.3
VO_2	—	—	—	—	n	0.5
V_2O_5	4.1	−0.18	—	—	n, (met.)	0.3
Cr	4.56	—	346.7	6.76	met.	—
CrO	—	—	—	—	p	—
Cr_2O_3	5.9	1.34	—	—	p, (n)	1.9
CrO_2	—	—	—	—	n, (met.)	0.3
CrO_3	—	—	—	—	n	3.2
Mo	4.21	—	672.0	7.35	met.	—
MoO_2	—	—	—	—	p	—
MoO_3	4.25	0.04	—	—	n	2.8
W	4.55	—	868.3	7.98	met.	—
WO_2	4.95	0.40	—	—	n	—
WO_3	4.5	−0.05	—	—	n	2.9
Mn	4.0	—	293.5	7.43	met.	—
MnO	6.5	2.5	—	—	n, (p)	1.25
Mn_2O_3	—	—	—	—	p	0.3
β-MnO_2	—	—	—	—	n	0.3
γ-MnO_2	—	—	—	—	n	0.6
Fe	4.6	—	415.8	7.90	met.	—
FeO	3.85	−0.75	—	—	p, (n)	0.4
Fe_3O_4	—	—	—	—	n, (p)	0.4
α-Fe_2O_3	—	—	—	—	n	1.9
β-Fe_2O_3	—	—	—	—	—	2.1
γ-Fe_2O_3	3.9	−0.70	—	—	n	2.2
Co	4.97	—	451.3	7.86	met.	—
CoO	—	—	—	—	p, (n)	0.8
Co_3O_4	4.9	−0.07	—	—	p	0.9
Co_2O_3	—	—	—	—	n	—
Ni	5.06	—	437.1	7.63	met.	—
NiO	5.55	0.49	—	—	p	1.9
Ni_2O_3	—	—	—	—	n	—
Ru	4.66	—	687.5	7.36	met.	—
RuO_2	—	—	—	—	met.	0.1
Rh	4.76	—	593.3	7.46	met.	—
Rh_2O_3	—	—	—	—	—	—
RhO_2	—	—	—	—	met.	—
Pd	4.98	—	400.3	8.33	met.	—
PdO	—	—	—	—	—	0.04
Os	4.55	—	749.8	8.7	met.	—
OsO_2	—	—	—	—	—	—
Ir	5.0	—	710.1	9.2	met.	—
IrO_2	—	—	—	—	met.	—
Pt	5.42	—	524.6	8.96	met.	—
PtO	—	—	—	—	—	—
Pt_3O_4	—	—	—	—	—	—
PtO_2	—	—	—	—	n	—

Symbols: ϕ is the work function, $\Delta H^{\circ}_{f,298}$ is the sublimation energy, I is the ionisation energy, W is the width of the forbidden energy gap, and met. denotes metallic conduction. *The brackets denote a conductivity type not confirmed independently.

In general the rate-limiting step in the oxidation of metals whose oxides are electronic conductors is the breaking of bonds in the crystal lattice of the metal. If the oxide has a mixed (ionic–electronic) or an ionic conduction (as in Nb, Ta, and Zr) the transport of electrons through the oxide layer can be rate-limiting. Unfortunately, very little information is available on the activation energies for conduction and self-diffusion of metal ions in oxides containing metals in different states of oxidation.

Activation energies for conduction and metal diffusion in oxides measured at high temperatures are listed in Table 3. We can distinguish the group of electronic semiconductors (the oxides of Mn, Fe, Co, Ni, Cu) for which the activation energy for conduction is $E_{\sigma} < 83.7$–125.6 kJ mole^{-1} and the activation energy for the diffusion of the cation is $E_d < 210$ kJ mole^{-1}. Metals of this group show the characteristic relationship between the rate of oxidative dissolution and the sublimation energy of the metal[16]. In the case of the electronic semiconductors TiO_2, WO_3, and Ta_2O_5 and of the semiconductors of mixed or ionic type Nb_2O_5 and ZrO_2, which have relatively high values of E_{σ} (>83.7–125.6 kJ mole^{-1}) and of E_d (>209.3 kJ mole^{-1}), the oxidation of the metal is slow[16].

The stability of the oxide formed on the metal surface towards the replacement of oxygen by another counter-ion (for example, Cl^-) generated by electron transfer from the metal to the components of the donor–acceptor medium plays an important role in the oxidative dissolution of metals. Obviously, if the stability of the oxide is higher than that of the corresponding chloride (allowing for the effects of complex formation on the surface and in the solution) the dissolution will be suppressed.

Table 4 gives the standard heats of formation ΔH°_{298} of the chlorides and oxides of some transition metals. We note that the metals can be divided into two groups with respect to the relative stability of the corresponding oxides and chlorides (for the same degree of oxidation):

1) Co(III), Mn(IV), Cr(III), Fe(III), Mo(IV, VI), Ti(III, IV), V(III, IV, V), W(VI), Nb(V), Ta(V), Zr(IV), Rh(I, III), and Ru(IV) (chlorides less stable than oxides);

2) Ag(I), Au(I, III), Co(II), Ni(II), Mn(II), Pd(II), Cr(II), Fe(II), and V(II) (chlorides more stable than oxides).

The importance of the relative stability of the lower and the higher chlorides and oxides should be stressed. During the transfer of an electron from the metal to the oxide surface the metal ions in the oxide are reduced, and the stability of the oxides of the first group of metals decreases ("destabilisation" of the oxide layer): this improves the conduction properties of the layer, and the reactions leading to the formation of metal chlorides and their complexes become energetically preferred. If atmospheric oxygen is present in the system the degree of oxidation of the metal in the oxide layer increases, and the rate of formation of chlorides or oxide chlorides decreases. Under these conditions the rate of the oxidative dissolution process can be a function of the rate of the relevant rate-limiting step: either the supply (by diffusion) of oxygen to the surface or the dissolution of the oxide in the liquid phase containing chloride ions.

For the metals in the second group the characteristic reaction is the replacement of oxygen by chlorine: "stabilisation" of the oxide layer is produced by the oxidation of the metal ions by oxygen in the oxide layer, i.e. by the formation of higher oxides. This lowers the rate of the oxidation. The addition of oxygen to the donor–acceptor system suppresses the reaction in the first case and assists it in the second[9,16].

We note that the rate of dissolution of oxides depends less on the concentration of oxidiser than on the nature and concentration of the complex-forming ligand. For example, in spite of the relatively low concentration of proton oxidiser, the rate of dissolution of BeO is much greater in oxalic acid than in hydrochloric acid[66].

3. The Oxide Layer on the Surface of a Transition Metal as a Carrier of Electrons from the Metal to the Acceptor

Compounds of the transition metals such as the oxides have a characteristic valence band due to metal ions in an intermediate state of oxidation, for example M^{2+}, and not to O^{2-} ions, since the M^{2+} level is 5–8 eV higher than the O^{2-} level. In these compounds holes are formed more readily in the high

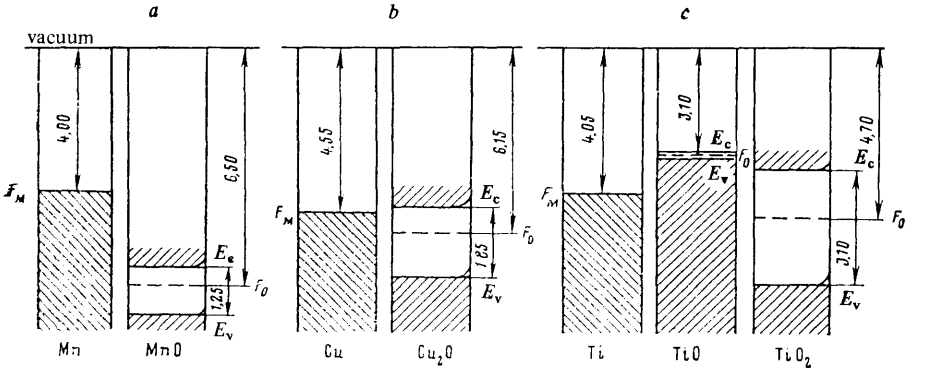


Figure 2. Energy level diagram (eV) for metals and their oxides: *a*) Mn/MnO, *b*) Cu/Cu_2O, *c*) $Ti/TiO/TiO_2$;[51-57] F_M and F_0 are the Fermi levels in the metal and the oxide, E_V and E_C are the edges of the valence and of the conduction band.

M^{2+} level or in the V'_M or V''_M levels (where V'_M and V''_M are vacancies with a negative and a double negative effective charge respectively). In any case, the emission of electrons from the M^{2+} level in transition metals[67] has an energy advantage equal to double the quantity $\Delta E_{OM} = E_O^{2-} - E_M^{2+}$. Thus, since the oxygen 2*p* band in transition metal oxides lies below the valance band of the metal, the first possible electron transition to give a polar state is (for nickel, say) from the Ni^{2+} ($3d^8$) to the Ni^+ ($3d^9$) band by the reaction[68]

$$Ni^{2+} + Ni^{2+} + h\nu \rightarrow Ni^{3+} + Ni^+ \qquad (4)$$

Table 3. Activation energies for conduction (E_σ) and for diffusion (E_d) of cations in metal oxides (kJ mole^{-1}).

Metal oxide	E_σ	E_d
TiO_2 [57]	106.3÷152.8	257.1
V_2O_3 [57]	31.0	—
V_2O_5 [57]	19.3÷96.7÷28.9	—
Cr_2O_3 [57]	19.3÷154.5÷47.3	—
CrO_2 [57]	19.3	—
MnO [58]	35.6	125.6÷146.5
Mn_3O_4 [57]	56.1	—
MnO_2 [57]	28.9	—
FeO [57]	32.7	—
Fe_3O_4 [59]	7.5÷28.9÷19.3	124.3
CaO [60]	64.9÷28.9	144.4÷160.8
NiO [61]	90.0; 75.4	182.1
Cu_2O [62]	15.5÷24.3; 25.1÷33.5	151.1
CuO [57]	67.8	—
WO_3 [57]	57.8; 159.1	—
ZrO_2 [63]	—	—
Nb_2O_5 [64]	125.6÷159.1	—
Ta_2O_5 [65]	209.3	—

Notes: The width of the forbidden gap is 2.0 eV for ZrO_2 and 2.2 eV for Nb_2O_5,[57] with mixed conductivity; the energy gap for Ta_2O_5 is 3.6 eV.[57]

This transition is dipolar, and allowed by the selection rules[69], since it is from a $^3F(3d^8)$ to a $^2D(3d^9)$ state. On the other hand a transition from the $O^{2-}(2p^6\text{-}^1S)$ to the $Ni^+(^2D)$ band is either forbidden by the selection rules or (if treated as quadrupolar) it should have a much lower intensity[70].

Whereas reduction of a non-transition metal (M^{3+}) causes electrons to appear at the M^{2+} level, and oxidation produces holes in the O^{2-} band, in the oxides of transition metals (for example, in magnetite, Fe_3O_4) both processes are accommodated in the M^{2+} band, which is half-filled.

Table 4. Standard heats of formation ΔH°_{298} (kJ mole^{-1}) of the chlorides and oxides of the transition metals.

Chlorides	$-\Delta H^\circ_{298}$	Oxides	$-\Delta H^\circ_{298}$
AgCl	127.0	Ag_2O	30.6
—	—	(Ag_2S)	29.3
AuCl	35.2	—	—
$AuCl_3$	118.5	Au_2O_3	−80.9
$CoCl_2$	325.7	CoO	239.5
—	—	Co_3O_4	879.2
CuCl	134.8	Cu_2O	166.6
$CuCl_2$	206	CuO	155.3
$NiCl_2$	316.1	NiO	244.5
$MnCl_2$	482.7	MnO	388.5
—	—	MnO_2	521.3
$PdCl_2$	190.1	PdO	85.4
$CrCl_2$	395.9	CrO	272.1
$CrCl_3$	563.5	Cr_2O_3	1129.2
$MoCl_4$	479.8	MoO_2	589.5
$MoCl_5$	529.6	—	—
$MoOCl_4$	644.8	MoO_3	754.9
MoO_2Cl_2	724.3	—	—
$FeCl_2$	341.2	FeO*	266.7
$FeCl_3$	405.3	Fe_3O_4**	1117.9
$TiCl_3$	714.7	TiO	525.0
$TiCl_4$	800.5	Ti_2O_3	1519.0
$TiOCl_2$	765.3	TiO_2***	941.6
VCl_2	452.2	VO	427.5
VCl_3	573.6	V_2O_3	1256.0
$VOCl_3$	720.1	V_2O_5	1561.1
VCl_4	577.8	V_3O_5	1574.2
WCl_5	573.6	WO_2	570.7
WCl_6	682.5	WO_3	840.9
WO_2Cl_2	837.4	—	—
$WOCl_4$	745.3	—	—
$NbCl_5$	798.0	Nb_2O_5	1904.2
$NbOCl_3$	880.1	—	—
$TaCl_5$	862.5	Ta_2O_5	2046.5
$ZrCl_4$	963.0	ZrO_2	1081.0
RhCl	67.0	RhO	90.9
$RhCl_3$	234.5	Rh_2O_3	286.0
$RuCl_3$	205.2	RuO_2	305.6

*Wüstite.
**Magnetite.
***Rutile.

From these considerations we can formulate the main features of the oxidation of transition metals in the liquid phase with allowance for the catalytic role of the oxide film in the transfer of an electron from the metal to the oxidiser.

1. The oxide film on the metal surface acts as a catalyst§ for the oxidation of a transition metal in the liquid phase. Metal ions in the oxide film are reduced by the electrons flowing from the metal under the influence of the oxidiser¶ adsorbed on the surface. The adsorption of oxygen on the surface of a thin oxide layer produces a negative charge in the film. The outer surface of the oxide receives electrons both from the bulk of the film and from the metal, and the metal acquires a positive charge relative to the film[71]. Transition metals in a lower state of oxidation show a characteristic tendency to form metal–metal bonds, especially in the lower halides and oxides of Nb, Ta, Mo, W, and Re, though at least one such compound is known for every element of the *d* group[72]. We may assume that electron transfer is produced either by the formation of clusters in the lattice of transition-metal lower oxides containing M–M bonds with an energy similar to the bond energy of the transition metal lattice[73], or through the 2*p* band of the oxygen sublattice, which allows continuous exchange of electrons between the iron ions through the oxygen ions[74].

2. A metal atom incorporated into the crystal lattice loses enough electrons to convert it into its stable lower state of oxidation, for example

$$Cu^0 - e \rightarrow Cu^I; \quad Fe^0 - 2e \rightarrow Fe^{II}.$$

3. As a result of the donor–acceptor properties of the complex on the surface the reduction of the metal ions in the film is accompanied by a stimulated, synchronous transfer of electrons to the conduction band, yielding a pair of metal ions in states of oxidation differing by two units [see Eqn.(4)].[67,75] Since the postulate of a purely ionic bond in transition metal oxides is only a rough approximation we cannot exclude the interaction between the oxidiser and a virtual Mott exciton as the mechanism of this process. The formation of ions in different states of oxidation at very short distances apart may be equivalent to the formation of an active centre (which consists of a number of pairs of these ions, i.e. a cluster)[76].

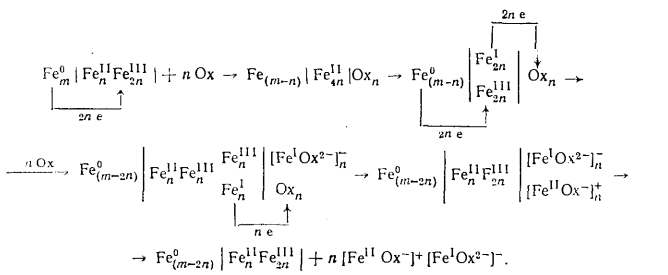
4. Stabilisation of the excited state of the ions (or ion) is obtained by the transfer of one or two electrons from the surface of the oxide layer to the oxidiser, and depends on the nature of the latter (one-electron or two-electron acceptor).

5. Stabilisation of the counter-ions takes place through the formation of neutral complexes (for example, $[M^{n+}Ox_n^-]^0$, $[M^{2n+}Ox_n^{2-}]^0$), or of an ionic complex of the type $[M^{n+}Ox_{(n-m)}^-]_p^{m+} \cdot [M^{n+}Ox_{(n+p)}^-]_m^{-p}$ in the solvated state, which assists the diffusion of the complex into the solution.

6. Diffusion of an oxidised metal ion into the solution in the form of a neutral complex takes place when the stability of the complex is higher than the stability of the oxide on the surface, since this process requires the breaking of M–O bonds and formation of new M–Ox bonds.

7. Saturation of the free valencies of the oxygen atoms on the surface takes place through the diffusion of metal ions along vacancies in the layer by the replacement pressure ("crowdion") mechanism[77].

According to the proposed mechanism, the oxidation of metals can be described by the following scheme (in which the metal is a two-electron donor, iron (Fe^0), the oxidiser is a one-electron or two-electron acceptor, and the vertical lines denote the boundaries of the oxide phases):



In this process the oxidised state of the layer is regenerated. The scheme allows the formation of univalent iron, stabilised in an ionic complex by bivalent iron.

Evidently, further oxidation of the complex can take place in solution. However, further oxidation on the surface is also possible, giving Fe(II)–Fe(III) iron complexes of different valency in which the stabilisation of the bivalent iron[10] depends on the donor–acceptor properties of the solvent included as a ligand in the complex cation (for example, $[Fe^{II}(CH_3CN)_6].[Fe^{III}Cl_4]_2$) or in the complex anion (for example, *cis*-$[Fe^{III}Cl_2(DMSO)_4]_2[Fe^{II}Cl_4]$).

As the scheme shows, the active centre on which the oxidation takes place contains at least two metal atoms (or ions).

Inspection of the catalytic properties of oxide layers of the transition metals in the light of the above mechanism reveals the possibility (in principle) of selective oxidation of the transition metals. The basis of the selective oxidation process is the requirement of complementarity of the reaction† *with respect to the active centre*, i.e. the retention of the one- or two-electron mechanisms for the electron transfer to the oxidiser, irrespective of the number of electrons removed in the stabilisation of an atom from the crystal lattice of the metal. The realisation of this process depends on the properties of the complex on the metal surface (or on those of the oxide layer), i.e. on the possibility of redistributing the electron density in the surface complex by transferring one or two electrons. This redistribution leads to the decomposition of the complex, giving oxidised forms of the metal in solution in a lower state of oxidation than the ions on the metal surface (for example, those in the oxide layer). Several examples consistent with this interpretation of the role of the film on the metal surface can be quoted.

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§ We shall use the term "catalyst" to denote a compound formed on the surface from the metal ion newly created in the oxidation process and from the O^{2-} ion set free, so that the "composition" of the compounds on the surface stays constant but its constituent metal ions are replaced.

¶ The term "oxidiser" (Ox) refers to a complex (or association) between the components of a donor–acceptor system in the liquid phase, for example $(DMFA)_n(RX)_m$.[23,24]

† A reaction is called complementary or non-complementary depending on whether the oxidation states of the oxidiser and of the reducer change by the same amount. The complementarity (or electronic correspondence) principle states that the replacement of a non-complementary by a complementary process leads to a faster reaction[78,79].

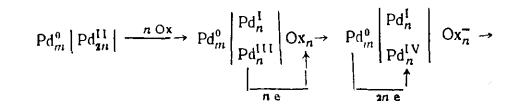
A study[80] of the cathodic reduction of oxide layers on an iron surface has shown that the outer layer of oxide contains ions in a higher state of oxidation, and that its oxygen content is higher than the stoichiometric composition Fe_2O_3 (oxide with an excess of cation vacancies).

We also know that the removal into an acid medium of the higher-valancy oxide from an iron surface involves the reductive dissolution rather than the direct dissolution of hematite and magnetite. A study of the solubility of the oxide Fe_2O_3 showed[81] that the direct action of acid on this oxide is slow, and gives Fe^{2+} ions in solution, though the oxide formally consists of Fe_2O_3. In a short-circuited model cell consisting of Fe_2O_3 and Fe^0 the iron was found to be the anode, and the oxide the cathode. Under these conditions the transfer of an electron from the metal to the oxide leads to the formation of structure defects of Fe^{3+} in the oxide lattice (i.e. to an increased concentration of Fe^{2+}). The appearance of Fe^{2+} ions upon dissolution of an oxide containing only Fe^{3+} is explained by assuming that the dissolution is confined to the structure defects. This explanation is consistent with our mechanism of electron transfer from the metal to the oxidiser through a layer of oxide.

It has been shown[82,83] that the transfer of an ion from the surface to the solution is assisted by a decrease in its valency. In the dissolution of precious metals in the presence of strong-field complexing ligands (for example, the dissolution of gold by the cyanide method with oxygen as the oxidiser, see p.12 of Ref.48) a layer of intermediate products is formed (mainly, the thermodynamically unstable[48] higher oxide of gold(III), Au_2O_3), and the cyanide complex of univalent gold goes into solution[2]. The thickness of this layer varies from 100 (on silver) to 1000 conventional monolayers (on copper), and depends on the concentration of cyanide and oxygen, on the rate of stirring, and on the temperature and duration of the reaction. It has been stressed[82,83] that the exact mechanism of action of these films is not understood, though their permeability to oxygen has been established. The rate of dissolution of the film itself plays an important part in the metal oxidation process.

A dynamic equilibrium is created on the surface, and the film adopts a constant thickness, depending on the conditions of the reaction[84].

The complementarity of the oxidation process with respect to the active centre which we have postulated can be further tested by considering the oxidation of a platinum group metal in which the metal is a two-electron donor (palladium) and the oxidiser is a one-electron acceptor:



As a rule the oxidation of Pd^0 with a two-electron acceptor produces a slower reaction, despite the fact that Pd^0 is a two-electron donor. The reaction follows a one-electron mechanism because the active centre formed on the surface is a one-electron donor.

The above considerations lead to the conclusion that the oxidation can be accelerated by adding to the system a compound able to act simultaneously as a one- and two-electron oxidiser and reducer[79]. Thus a much faster reaction is obtained by adding to the oxidation–reduction system a catalytic carrier which converts the one-electron electron-transfer mechanism into a two-electron mechanism (catalytic carrier, copper and iron ions (M); oxidiser, molecular oxygen)[85,86]:

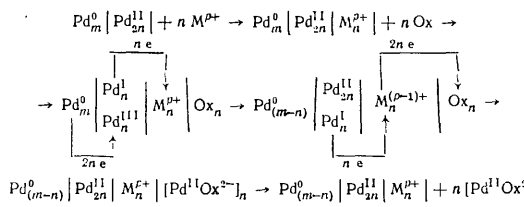


Table 5. Characteristics of electron transfer from a metal through an oxide layer to an oxidiser.

Surface reaction	Number of electrons*				E/E'	$\Delta E_i = E_i - E_i'$	Optimum conditions ($\Delta E_i < 0$)	Element	E_i/E_i'	ΔE_i, eV
	M^0	M^n	M^{n-1}	Ox						
$M^0 + 2M^n \rightarrow M^{2+} + 2M^{n-1}$ (5)	2	1	2	2	$\frac{W + I_0 + I_+ + I_{n-2} - I_{n-1}}{I_0 + I_+}$	$W + I_{n-2} - I_{n-1}$	$W < I_{n-1} - I_{n-2}$	Fe	$\frac{W + 9.7}{24.1}$	$W - 14.4$
$M^0 + M^n \rightarrow M^{2+} + M^{n-2}$ (6)	2	2	2	2	$\frac{W + I_0 + I_+ + \frac{1}{2}[I_{n-2} + I_{n-3}]}{I_0 + I_+ + I_{n-2}}$	$W + \frac{1}{2}[I_{n-3} - I_{n-2}]$	$W < \frac{1}{2}[I_{n-2} - I_{n-3}]$	Fe	$\frac{W + 36.15}{40.3}$	$W - 4.15$
$2M^0 + M^n \rightarrow 2M^+ + M^{n-2}$ (7)	1	2	1	1	$\frac{W + 2I_0 + I_{2+} - I_{n-1} + I_{n-2}}{I_0 + \frac{1}{2}[I_+ + I_{2+} - I_{n-1} - I_{n-2}]}$	$W + I_0 + \frac{1}{2}[I_{2+} - I_0 - I_{n-1} - I_{n-2}]$	$W < \frac{1}{2}[I_+ + I_{n-1} + I_{n-2} - I_{2+}] - I_0$	Au	$\frac{W - 2.1}{9.2}$	$W - 11.2$
$M^0 + M^n \rightarrow M^+ + M^{n-1}$ (8)	1	1	1	1	$\frac{W + I_0 + \frac{1}{2}[I_{n-1} - I_{n-2}]}{I_0}$	$W + \frac{1}{2}[I_{n-1} - I_{n-2}]$	$W < \frac{1}{2}[I_{n-2} - I_{n-1}]$	Au	$\frac{W + 13.95}{9.2}$	$W + 4.75$

Symbols: I_0 is the ionisation energy (eV) of the neutral unexcited atom by the reaction $M^0 \rightarrow M^+ + e$; I_+ is the ionisation energy (eV) of the singly charged (positive) unexcited metal ion by the reaction $M^+ \rightarrow M^{2+} + e$; $I_{(n-1)}$ is the ionisation energy (eV) of the unexcited metal ion with $(n - 1)$ positive charges by the reaction $M^{n-1} \rightarrow M^{n-2}$; W is the width of the forbidden energy gap (eV); E is the energy required for the electron transfer process with allowance for the formation of an electron–hole pair; E' is the same energy without the correction for the formation of an electron–hole pair.
*The numbers of electrons taking part in the catalytic process in the oxide layer are shown; M^0 is the metal (electron donor), M^n is the metal ion (electron acceptor), M^{n-1} is an active centre (electron donor), Ox is the electron acceptor in the liquid phase.

4. Role of the Surface Oxide Film as an Intermediate Electron Trap

The role of the surface as a direct participant in a chemical reaction, and in particular the metal oxidation reaction, includes the provision of a site for the localisation of free current carriers and excitons, since the Madelung constant (μ) on the surface is smaller than in the bulk, and therefore an electron–hole pair (or exciton) has a lower energy on the surface. In the case of an ionic cubic lattice we have $\mu = 1.74$ for the bulk and $\mu = 1.68$ for the surface, which is the cause of excition transport from the surface[97].

It can be shown that the oxidation of a metal covered with a layer of a semiconducting compound of variable composition and containing ions of the metal in different states of oxidation (e.g. an oxide) is energetically more favourable if it takes place through the formation of an electron–hole pair than by direct oxidation without preliminary excitation of the atoms (or ions). If all the other conditions stay the same (composition of the oxidation–reduction medium, composition of the layer on the metal surface, Madelung energy) two alternative paths are available for the oxidation of iron.

1) Oxidation through the formation of an electron–hole pair (in the case of a two-electron mechanism for the transport of electrons to the oxidiser):

a) reduction of Fe_3O_4 to FeO

$$Fe^0 + 2Fe^{3+},\ (Fe^{2+}) \rightarrow 3Fe^{2+},\ (Fe^{2+}) + E_v$$
$$E_v = I_0 + I_+ - 2I_{2+} = 7.9 + 16.2 + 2 \cdot 30.6 = -37.1\ \text{eV}$$

b) formation of an electron–hole pair

$$2Fe^{2+} \rightarrow Fe^+ + Fe^{3+} + W\ ,$$

where W is the width of the forbidden energy gap for FeO (Fe_3O_4) = 0.4 eV (see Table 2)

c) oxidation of Fe^+

$$Fe^+ \rightarrow Fe^{3+} + 2e + E_{OC}$$
$$E_{OC} = I_+ + I_{2+} = 16.2 + 30.6 = 46.8\ \text{eV}\ .$$

The total energy requirements of the first path are

$$E = E_v + W + E_{OC} = -37.1 + 0.4 + 46.8 = 10.1\ \text{eV}.$$

2) Oxidation without formation of an electron–hole pair, replacing the two-step process (b), (c) by the oxidation of two Fe^{2+} ions:

d) $$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e + E'_{OC}$$
$$E'_{OC} = 2I_{2+} = 2 \cdot 30.6 = 61.2\ \text{eV}$$
$$E' = E_v + E'_{OC} = -37.1 + 61.2 = 24.1\ \text{eV}\ .$$

The gain in energy $\Delta E = E - E'$

$$\Delta E = 10.1 - 24.1 = -14.0\ \text{eV}.$$

In idealised limiting cases of oxidation in the absence of oxygen and of an oxide layer on the metal surface, or of a rate of dissolution of the oxide layer in the donor–acceptor medium greater than the rate of oxidation of the metal, the complex formed by the components of the liquid phase with the surface atoms of the metal can also be a catalyst for the oxidation process if it can be treated as a semiconductor. We can assume that the lower the activation energy for conduction and the energy gap in the complex, the more marked will be the catalytic effect.

Calculated values of the energy required for the electron transfer process in the film on a metal surface are shown in Table 5 for a one-electron (e.g. Au^0) and a two-electron donor metal (e.g. Fe^0), without allowance for the electron affinity of the oxidiser or for the solvation energies of the initial and the final products, which are assumed constant.

If the metal ions present in the film in a higher state of oxidation act as one-electron acceptors [for example, according to reaction (5)] the energy gain for iron (with $W = 0.4$ eV) is 14 eV.

If the metal ions in a higher state of oxidation act as a two-electron acceptor in the film [for example, by reaction (6)] the energy gain for iron becomes (W – 4.15) eV. Since $W \leq 3$ eV for semiconductors, in this case the energy gain is >1 eV. Comparing the electron transfer systems (5) and (6), assuming in both cases the formation of electron–hole pairs, we conclude that the first path offers an energy advantage:

$$\Delta E_{1,2} = E_1 - E_2 = {}^1/_2(I_{n-2} - I_{n-3}) - I_{n-1}\ .$$

For iron $\Delta E_{1,2} = -26.45$ eV, i.e. the one-electron reduction of the metal ion in the higher state of oxidation is preferred in this case. A similar analysis for gold suggests that reaction (7) is preferred to reaction (8) as an electron transfer path ($\Delta E_{3,4} = -16.05$ eV), whereas for a process not involving the formation of an electron–hole pair the two reactions are energetically equivalent ($E'_3 = E'_4$)#.

Our analysis justifies the following conclusions.

1) The transfer of an electron from the metal to the oxidiser through the surface film is energetically more favourable (if the film has semiconductor properties) than the "normal" transport process found in oxidation–reduction reactions in the liquid phase.

2) the most favourable process in terms of energy is the transfer of an electron through a layer of oxide with a very small decrease in the degree of oxidation of the metal ions in the layer [Table 5, Eqns.(5), (6), and (7), (8)].

V. ROLE OF SURFACE DEFECTS

A real surface differs from an idealised surface by perturbations in the periodicity of the structure, i.e. by the presence of surface defects[88]. The defects can participate directly in surface processes, since they can act as centres for the coordination of the components of the donor–acceptor medium. Vacancies in the cation sublattice may also play a part in the formation of electron–hole pairs by the quasi-chemical equation

$$V^0_M + V''_M \rightleftarrows (V'_M, h)^{\bullet} + (V'_M, e)'' \rightleftarrows 2V'_M + h + e$$

where V^0_M, V'_M, and V''_M are vacancies with a zero, a negative, and a double negative effective charge.

Transition metals containing *d* electrons and able to transfer electrons reversibly form characteristic associations (or complexes) of defects of the same kind because the attractive forces arising from quantum-mechanical exchange interaction are large enough to overcome the elastic and Coulombic interactions.

In the non-stiochiometric lower oxide of iron the holes, which are localised on iron ions as Fe^{3+}, can interact with the cation vacancies bearing an effective negative charge. This interaction leads to the formation of a composite complex defect: an interstitial ion bound to two vacancies, $[V'_{Fe}Fe^{3+}V''_{Fe}]'$. A complex with this configuration is more stable than the simple vacancy; it is a structure element of the phase $Fe_{3-y}O_4$ into

For gold $I_+ + I_2 - I_{n-1} - I_{n-2} = 0$ (see Table 5).

which $Fe_{1-y}O$ is converted when the critical metal deficit is exceeded. In these oxides the defects show long-range order, and the electrical conductivity is abnormally large (125 $Ohm^{-1}\,cm^{-1}$).[89] It has been suggested[90] that under these conditions the conductivity is due to the exchange of electrons between two adjacent iron ions (Fe^{2+} and Fe^{3+}). Evidently, analogous effects are possible in other oxide phases with a metal defect, $[M_{1-y}O]$, which include oxides with structure defects of the cation vacancy type[77] such as MnO, NiO, and Cu_2O.

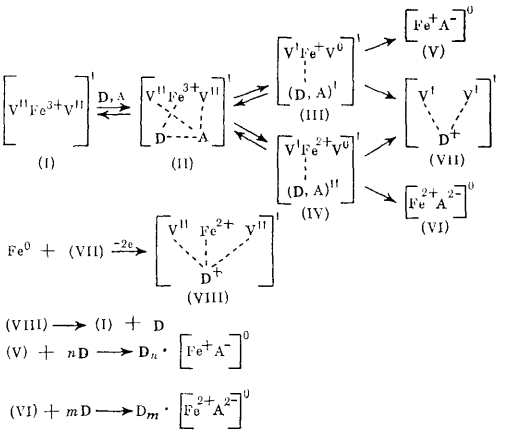
It has been shown that the active dissolution of iron covered with FeO involves an increase in the non-stoichiometry of the surface oxide and an increased concentration of surface defects: anion vacancies (Fe^{II} ions) and free electrons. Photoelectric polarisation measurements have established that the passivation of iron, copper, and silver is accompanied by changes in the surface oxide towards a stoichiometric composition, and by a decrease in the concentration of non-stoichiometric defects[88].

Experimental data[91,92] indicate the formation of the anion radicals ($Ox^{\pm}$) on the surface of metal oxides in the presence of acceptor molecules (O_2, SO_2, quinones). However, complex formation takes place mainly on charged surface defects (negatively ionised cation vacancies) rather than on ordinary lattice atoms, The assumption of charge transfer from an ionised defect to a molecule of the oxidiser is confirmed by the formation (for example, with benzoquinone or fluoranil) of charge-transfer complexes (CTC) of the same structure on both typical semiconductor (Ge, TiO_2, ZnO) and typical insulator surfaces (MgO, Al_2O_3).[93,94] For donor molecules the most probable coordination is on ordinary lattice atoms and on ions in interstitial sites.

Donor molecules (for example, triphenylamine) form cation radicals when adsorbed on zeolite surfaces, and acceptors such as tetracyanoethylene, trinitrobenzene (TNB), and *m*-dinitrobenzene form anion radicals. It is interesting to note that previous adsorption of donors (anthracene and perylene) on the zeolite causes a ten-fold increase in the number of TNB anion radicals as compared with the adsorption of TNB on a fresh zeolite surface[95]. Under these conditions an additional TNB anion radical is formed for every three anthracene or perylene cation radicals. This effect can be explained by the cooperative interaction of vacancies on a solid surface[95]. The adsorption of SO_2 and benzene leads to the formation of the corresponding ion radicals, i.e. $SO_2^{\pm}$ and $C_6H_6^{\pm}$. The adsorption of one oxygen molecule produces one perylene cation radical, but $O_2^{\pm}$ is not formed under these conditions. We interpret this as evidence of the cooperative nature of the interaction on the solid surface, since additional electron transport from the donor to the surface without involving an acceptor suggests a surface with a high capacity for electrons and controllable donor–acceptor properties.

Evidently, the formation of surface complexes in a donor–acceptor medium leads to electron transfer from the negative pole of the resulting dipolar MC (or CTC) to an ordinary lattice atom or ion, and from the vacancies to the positive end of the dipole. The formation of this coordination bond is accompanied by substantial changes in crystal field, with corresponding changes in the parameters of the defects, causing localisation of free carriers on the defects closest to the molecules held by coordination forces. This influences the strength of the bonds and the distortion in the complex, and weakens the intramolecular bonds of the MC. As a result of this coordination and collective interaction effect the localisation of holes near a metal ion in the lower state of oxidation and the emission of the ion from the surface into the liquid phase can take place within a unified quantum-mechanical system.

The participation of surface defects in complex formation with the oxidised form of the metal can be described (in the case of iron) by the following scheme:

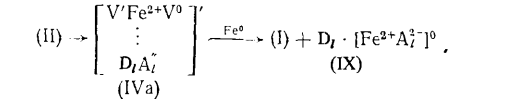


In step (9) the complex (II) is formed on the surface. It includes the components of the oxidation–reduction system (the donor D and the acceptor A), the metal ion, and defects with double negative charges. This is followed by redistribution of the charge density in the complex, in which the charge on the active centre is retained. In the ground state the two components of the complex are bound by ion–dipole, hydrogen, and dispersion forces, and also (to a small extent) by electrostatic and covalent forces arising from electron transfer from DA to the metal. This transfer is largely determined by the electronegativity of the metal and also by the donor–acceptor properties and by the polarisability of the components of the medium (strictly speaking, of their associations) involved in complex formation on the surface. Depending on the relative stability of the complexes (III) and (IV), and on the donor–acceptor properties of DA, neutral complexes of univalent and of bivalent iron [(V) and (VI)] will diffuse into the solution. This stabilises the cation vacancy complex (VII) containing a positively ionised molecule of the donor [step (9)]. Two-electron transfer from a metal atom to the complex (VII) causes the donor to be transferred to the solution [steps (10) and (11)] and regenerates the active centre I.

This scheme ignores the redistribution of electron density in the complex on the surface, which can lead to a weakening of the intramolecular bonds and to the ejection of fragments of the donor (D_f) and of the acceptor (A_f) by the reaction

$$(II) \rightarrow D_f + A_f . \qquad (12)$$

Reaction (13) brings into the solution the complex (IX) between the metal and the decomposition products of the oxidation–reduction system:



The reaction

$$(II) \rightarrow (IVa) \rightarrow (I) + D_l + A_l \qquad (14)$$

causes catalytic conversion of the components of the donor–acceptor system: in other words, the metal surface can stimulate (or accelerate) the interaction between D and A with

formation of the fragments D_f, D_l, A_f, and A_l. This reaction path does not lead to oxidation of the metal, and may even suppress it.

The possibility of controlling the direction of the interaction between a metal surface and the components of the liquid phase offers a real prospect of achieving selective oxidation of the transition metals.

VI. PROSPECTS OF OXIDATIVE DISSOLUTION AS A DIRECT METHOD OF SYNTHESIS OF TRANSITION METAL COMPLEXES IN THE LIQUID PHASE

The traditional methods of dissolving transition metals in a liquid phase, which give oxidised forms of the metal, rely on the use of aqueous media containing strong oxidising agents. The range of complexes which can be obtained in this type of system is very narrow, and the method is unsuitable for the direct (single-stage) synthesis of complexes by reaction (1).

Developments in the chemistry of the coordination compounds of transition metals have stimulated new approaches, based on non-aqueous aprotic media. The interest in these media stems mainly from the wide range of physicochemical properties which they offer: 1) their dielectric constants ε cover the range from 2.2 (1,4-dioxan) to 182 (*N*-methylformamide), 2) the dipole moments μ lie between 1.75 (tetrahydrofuran, THF) and 5.39 (hexamethyl phosphorotriamide, HMPA), 3) the region of existence of the liquid phase extends from −48.8 to +242 °C (for propylene glycol carbonate, PC), 4) these media offer specific donor–acceptor properties§, the *DN* varying from 2.7 (nitromethane) to 28.8 (HMPA) and the *AN* varying from 3.9 (diethyl ether) to 20.5 (nitromethane).

As we have shown[1], donor–acceptor systems containing dipolar aprotic compounds can be very effective in the oxidative dissolution of transition metals: dimethylsulphoxide, dimethylformamide, dimethylacetamide (DMA), tetramethylenesulphone (TMS), 2,4-dimethyltetramethylenesulphone (DMTMS), ethylene glycol carbonate (EC), PC, HMPA, acetonitrile (AN), benzonitrile (BN), and halogenated hydrocarbons (for example, CCl_4).[97] The most distinguishing feature of these organic solvents is their ability to form molecular complexes or associations[24]. This property also favours any thermodynamically allowed process¶ in which an easily polarisable solvent[104] acts as a bridging ligand and thus makes possible the transfer of an electron from the surface to an acceptor[25,105].

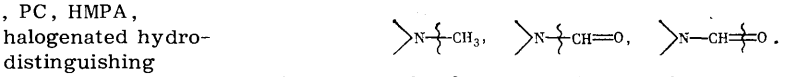
The oxidative dissolution of metals can yield two types of complex: neutral or ionic. The complexes may contain (as ligands) the components of the medium in their original state, or intermediate products formed by the interaction of these components[16,23,106].

1. Neutral complexes with an unchanged component as ligand. This case is most often met with copper, nickel, cobalt, molybdenum, and tungsten. Examples of complexes which have been synthesised in this way include the compounds L_2MX_2 (where M = Cu, Co, Ni) and $L_2MO_2X_2$ (where M = Mo, W), with X = halogen and L = DMFA, DMA, DMSO, and AN.

2. Ionic complexes with an unchanged component as ligand. Examples of complexes of this type which have been synthesised include the iron and cobalt compounds *cis*- and *trans*-$[Fe^{III}(DMFA)_4Cl_2][Fe^{III}Cl_4]$, $Fe^{III}(DMFA)_3Cl_2][Fe^{III}Cl_4]$, *cis*- and *trans*-$[Fe^{III}(DMSO)_4Cl_2]Cl$, $[Fe^{III}(DMSO)_3Cl_2].[Fe^{III}Cl_4]$, *trans*-$[Fe^{III}(DMSO)_4Cl_2][Fe^{III}Cl_4]$, *cis*-$[Fe^{III}.(DMSO)_4Cl_2]_2[Fe^{II}Cl_4]$, $[Fe^{III}(DMSO)_5Cl][Fe^{III}Cl_4]_2$, $[Fe^{II}(AN)_6][Fe^{III}Cl_4]_2$, $[Fe^{II}(BN)_6][Fe^{III}Cl_4]_2$, and $[Co^{II}.(DMSO)_6][Co^{II}Cl_4]$.

Further examples may be quoted to illustrate the special features of the direct method of synthesis. The metal being oxidised stimulates the interaction between the components of the oxidising system. The intermediates formed during the reaction are stabilised by ionic or coordination interaction with the metal ion. The possibility of including these "fragments" as ligands can lead to the formation of unusual complexes, both neutral and ionic. Thus by oxidising metals with a system containing DMSO the following complexes have been obtained: with iron, $[Fe^{III}(DMSO)_5Cl][Fe^{II}_2Cl_6O]$,[106] and with palladium $[(CH_3)_2S]_2PdBr_2$,[107] showing that the $>S \rightarrow O$ bond is broken. Stabilisation of the intermediates formed by this reaction is found also in the complex $[(CH_3S)_3C][Fe^{III}Cl_4]$ formed by the oxidation of iron during chlorination of cyclohexane in the DMSO + CCl_4 system: the H_3C-S bond is broken in this reaction[108].

It is interesting to note that in the dinuclear bridge complex [*cis*-$Cu(DMFA)_2Cl_2]_2$ formed during the oxidation of copper, one of the DMFA molecules bound to the copper atom through oxygen is in an anomalous state, all its bonds being longer than those of the other DMFA molecule in the *cis*-position. This suggests a weakening of the bonds as a result of complex formation, and the possibility of dissociation of the DMFA molecule into fragments under the influence of temperature and of the medium[106]. In fact, the following complexes containing fragments of the DMFA molecule have been isolated and characterised in DMFA systems[109,110]: $[(CH_3)_2.NCH\}_2CCl][Fe^{III}(DMFA)_6][Fe^{III}Cl_4]_4$ and $[CH_3NH_3]_4[Fe^{II}Cl_6].H_2O$. The reaction involves bond breaking as follows:



As an example of the potential use of this method we may consider the complex dimethyldibenzylammonium tetrabromopalladate, obtained[107] in the $C_6H_5CH_2Br$ + DMFA system. In this case the $>N-CHO$ bond in DMFA is broken, and stabilisation of the "fragments" $(CH_3)_2N-$ and $C_6H_5CH_2-$ takes place in the $[(CH_3)_2N(C_6H_5CH_2)_2]^+$ cation.

The use of chelating ligands in aprotic dipolar solvent–halogenated hydrocarbon systems widents the range of complexes which can be synthesised by this method. In the presence of α,α'-dipyridyl (α-dipy), dimethylglyoxime (DMGH), 8-oxyquinoline (8-oxin H), acetylacetone (acac H), cyclo-octa-1,5-diene (COD) the following complexes have been obtained: (α-dipy)$NiCl_2$, $Ni(DMG)_2$, $Co(8\text{-oxin})_2(H_2O)_2$, $Co(\alpha\text{-dipy})(acac)_2$, $H[Co(DMG)_2Cl_2]$, $Cu(DMG)_2$, $Cu(acac)_2$, $[Cu(COD)Cl]_2$, (α-dipy)$PdBr_2$, (α-dipy)$PtBr_4$, etc.[111,112] Another promising direction is the direct synthesis of transition metal complexes by catalytic oxidation with oxygen. This process has been demonstrated for a group of metals including some platinum group metals (Pd^0 and Pt^0) with which oxygen behaves as a "stoichiometric" reagent[16].

In the $M^0 + O_2 + HX + L + Kt$ system, where L = DMFA, pyridine (Py), pyridine oxide (PyO), AN, trimethylamine oxide $(CH_3)_3NO$, or the salt of an onium base ($>\overset{|}{N}X$, $\rightarrow SX$,

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§ *DN* is the donor number and *AN* is the acceptor number on Gutman's scale[7,96].

¶ The Gibbs free energy (ΔG°_{298}) calculated for the reaction $Fe^0 + 2CCl_4 \rightarrow FeCl_2 + C_2Cl_6$ without allowing for complex formation is −229.4 kJ mole^{-1}.[98,103]

X = Cl, Br, I), and Kt = Fe, Cu, a series of palladium and platinum complexes has been synthesised. With [HX[> [L] ionic complexes were isolated in which the oxidised metal was in the anion, and the cation was produced from L by protonation (L = Py, PyO), hydrolysis (L = DMFA, AN), dissociation [L = $(C_2H_5)_3NHBr$, $(CH_3)_3SBr$], or protonation of the deoxygenated form of L[$(CH_3)_3NO \rightarrow (CH_3)_3N$ + [O]]. With [HX] < [L] neutral complexes were obtained, for example $(\alpha$-dipy$)PdCl_2$.[85,86]

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Our study of the possible mechanisms of electron transfer from a metal to an oxidiser during the liquid-phase oxidative dissolution of transition metals, allowing for the semiconductor properties of the oxide layer, for the adsorption of molecular oxygen, and for the donor–acceptor interaction between the components of the medium has identified both complementary and non-complementary processes for the oxidation of metals in organic complex-forming media by which a wide range of coordination compounds can be synthesised.

The oxidative dissolution of transition metals in organic media and the direct synthesis of complexes are currently attracting intensive study from which interesting developments can be expected from the practical as well as the scientific aspect[113–115].

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The Synthesis, Structure, and Reactions of 1,3-Oxathiacycloalkanes

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Data concerning the methods of synthesis, structure, and properties of 1,3-oxathiacycloalkanes are discussed. The modern ideas about steric structure, reactivity, and mechanisms of the reactions of 1,3-oxathiacycloalkanes in the liquid phase are surveyed and described systematically.
The bibliography includes 102 references.

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I. INTRODUCTION

The chemistry of 1,3-oxathiacycloalkanes has been developing vigorously during the last 10–15 years. These compounds proved to be of interest for stereochemical studies and are used in fine organic synthesis and in the synthesis of biologically active preparations.

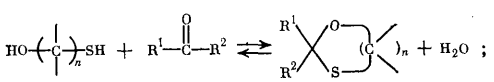
The problems associated with the chemistry of 1,3-oxathiacycloalkanes include selective methods of their synthesis from carbonyl compounds and mercaptoalkanols of different structure, the characteristics of their electronic and steric structure determined by the presence of oxygen and sulphur atoms in the 1- and 3-positions in the heterocycle, and their behaviour in reactions accompanied by the homolytic and heterolytic dissociation of the carbon–sulphur and carbon–oxygen bonds.

The aim of the present review is to give a systematic account and to survey the principal data concerning the synthesis, structure, and reactivity of 1,3-oxathiacycloalkanes in the liquid phase.

The gas-phase reactions of 1,3-oxathiacycloalkanes have been hardly investigated and the available data concern specific problems of heterogeneous catalysis and we have not considered them.

II. THE SYNTHESIS OF 1,3-OXATHIACYCLOALKANES

At the present time 1,3-oxathiacycloalkanes have been less thoroughly investigated than 1,3-dioxacycloalkanes and 1,3-oxazacycloalkanes. This is apparently due to the greater availability of diols and aminoalcohols compared with mercaptoalkanols. The vast majority of the 1,3-oxathiacycloalkanes described in the literature have been synthesised by the interaction of mercaptoalkanols with carbonyl compounds[1–21]:

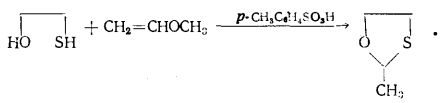


$n = 2, 3$.

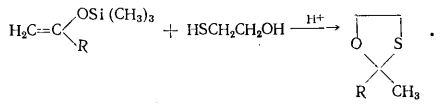
Various 1,3-oxathiolans[1–9] have been obtained by this method from 1,2-mercaptoalkanols and aldehydes or ketones[1–9] and 1,3-oxathianes have been obtained from 1,3-mercaptoalkanols[10–21].

Mercaptoalcohols condense in the presence of catalysts such as toluene-*p*-sulphonic acids, inorganic acids, and P_2O_5. Aldehydes and particularly formaldehyde give rise to 1,3-oxathiacycloalkanes in yields up to 90%, while in the case of ketones the yields are 30–70%.

Vinyl ethers can be used instead of carbonyl compounds[22,23]. Thus the condensation of mercaptoethanol with methyl vinyl ether yielded 2-methyl-1,3-oxathiolan[22]:

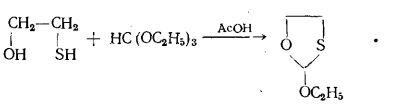


The reaction of trimethylsilyl vinyl ethers with 2-mercaptoethanol also leads to 1,3-oxathiolans[23]:



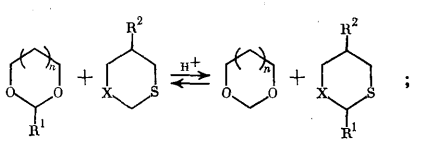
The yields reach 62–75% and are determined by the structure of the initial ether.

2-Ethoxy-1,3-oxathiolan has been synthesised by the reaction of 2-mercaptoethanol with ethyl orthoformate in the presence of acetic acid[24]:



2-Butyl-1,3-oxathiolan has been synthesised by the reaction of 2-ethoxy-1,3-oxathiolan with C_4H_9MgBr.[24]

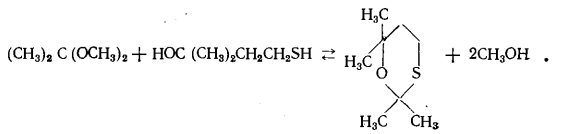
The possibility of obtaining 1,3-oxathianes as a result of the exchange reaction with 1,3-dioxacyclanes has been demonstrated[25–27]. This method makes it possible to obtain substituted 1,3-oxathianes which are difficult to synthesise by other methods:



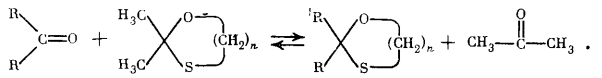
$n = 0, 1, 2$; X = O, S; $R^1 = CH_3$, C_2H_5, *n*-C_3H_7; $R^2 = H$, CH_3, iso-C_3H_7, iso-C_5H_{11}.

The yields are fairly high (79–95%). The reaction is catalysed by hydrochloric, sulphuric, and toluene-*p*-sulphonic acids and also by the KU-2 cation-exchange resin.

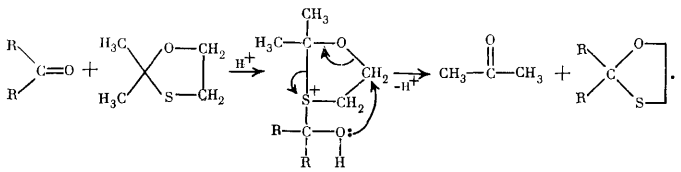
2,2,6,6-Tetramethyl-1,3-oxathiane has been obtained by the exchange acetalisation using the Dowex-50 catalyst[12]:



The synthesis of 2,2-disubstituted 1,3-oxathiacycloalkanes by the exchange reaction of 2,2-dimethyl-1,3-oxathiolan (or 2,2-dimethyl-1,3-oxathiane) with higher ketones has been described[1]:

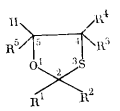


The yields reach 90%. The following reaction mechanism has been proposed:



The properties of certain five- and six-membered 1,3-oxathiacycloalkanes are presented in Tables 1 and 2.

Table 1. The properties of 1,3-oxathiolans



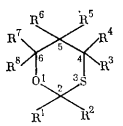
No.	R^1	R^2	R^3	R^4	R^5	B.p. °C (mmHg)	n_D^{20}	d_4^{20}	Refs.
1	H	H	H	H	H	55 (55)	1.5085	1.1656	[6]
2	CH_3	H	H	H	H	50 (30)	1.4852	1.0649	[6]
3	CH_3	CH_3	H	H	H	60 (67)	1.4724	—	[1, 6, 29]
4	C_2H_5	H	H	H	H	69—71 (43)	1.4828	1.0383	[6]
5	C_3H_7	H	H	H	H	85 (40)	1.4802	1.0129	[6]
6	iso-C_3H_7	H	H	H	H	83 (43)	1.4776	1.0090	[6]
7	C_6H_5	H	H	H	H	98—100 (1.3)	1.5850	—	[29]
8	C_2H_5	C_2H_5	H	H	H	105 (80)	1.4834	1.0039	[6]
9	CH_3	C_2H_5	H	H	H	12 (8)	1.4751	0.9776	[1]
10	H	H	CH_3	H	CH_3	75—78 (8)	1.4784	1.0444	[30]
11	CH_3	H	CH_3	H	CH_3	60—70 (9)*	1.466	0.9926	[30]
12	CH_3	CH_3	CH_3	H	CH_3	70—72 (9)*	1.4578	0.9531	[30]
13	CH_3	H	CH_3	CH_3	CH_3	80 (10)*	1.4603	—	[30]
14	H	H	H	H	CH_3	62—64 (64)	1.4877	1.0810	[28]
15	CH_3	H	H	H	CH_3	40—42 (35)*	1.434	1.0189	[28]
16	C_2H_5	H	H	H	CH_3	79—80 (58)*	1.4714	0.9900	[28]
17	C_3H_7	H	H	H	CH_3	88—89 (55)*	1.4654	0.9699	[28]
18	CH_3	CH_3	H	H	CH_3	42—44 (29)	1.4648	0.9788	[28]
19	C_2H_5	CH_3	H	H	CH_3	84—85 (74)*	1.4648	0.9825	[28]
20	iso-C_3H_7	CH_3	H	H	CH_3	95—97 (63)*	1.4670	0.9635	[28]
21	C_4H_9	CH_3	H	H	CH_3	106—108 (61)*	1.4700	0.9566	[28]
22	—$(CH_2)_5$—		H	H	H	106—107 (21)	1.5152	—	[23]
23	—$(CH_2)_6$—		H	H	H	135—140 (15)	1.5219	—	[23]
24	—$(CH_2)_4$—		H	H	H	103—107 (28)	1.5115	—	[23]
25	C_6H_5	CH_3	H	H	H	98 (1.3)	1.5640	—	[23, 29]
26	C_6H_5	C_6H_5	H	H	H	42—43	—	—	[1]
27	CH_3	C_2H_5	H	H	C_6H_5	104—105**	—	—	[9]
28	—$(CH_2)_5$—		H	H	C_6H_5	36—37**	—	—	[9]
29	—$(CH_2)_5$—		H	C_6H_5	C_6H_5	93—94**	—	—	[9]

* Mixture of isomers.
** Melting point.

III. THE STRUCTURE OF 1,3-OXATHIACYCLOALKANES

1,3-Oxathiacycloalkanes proved to be of interest for structural and kinetic studies. Firstly, the ring in these compounds is asymmetric, which increases the number of isomers. Secondly, the conformational effects in these compounds differ significiantly from those in symmetrical 1,3-dioxoacyclanes, since the bond lengths differ greatly: the lengths of the C—S, C—C, and C—O bonds are 1.82, 1.54, and 1.43 Å respectively. Thirdly, the electronegativity of the sulphur atom is much lower than that of the oxygen atom. The structure of 1,3-oxathiacycloalkanes has been investigated by ^1H NMR and the acid-catalysed equilibrium method.

Table 2. The properties of 1,3-oxathianes



No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	B.p., °C (mmHg)	n_D^{20}	Refs.
1	H	H	H	H	H	H	H	H	48 (11)	1.5026	[12]
2	CH_3	H	H	H	H	H	H	H	66—70 (24)	1.4922	[12]
3	H	H	H	H	H	H	CH_3	H	52—54 (13)	1.4920	[12]
4	H	H	H	CH_3	H	H	H	H	50—62 (12)	1.4903	[15]
5	H	H	H	H	CH_3	H	H	H	49—51 (8)	1.4939	[12]
6	C_2H_5	H	H	H	H	H	H	H	75—78 (19)	1.4856	[12]
7	iso-C_3H_7	H	H	H	H	H	H	H	75—78 (16)	1.4853	[12]
8	CH_3	CH_3	H	H	H	H	H	H	65—68 (17)	1.4890	[12]
9	H	H	CH_3	CH_3	H	H	H	H	73—75 (20)	—	[12]
10	H	H	H	H	H	H	CH_3	CH_3	53—55 (6)	1.4918	[12]
11	CH_3	CH_3	H	H	H	CH_3	H	H	55—57 (12)	1.4789	[12]
12	CH_3	CH_3	CH_3	H	H	H	H	H	60—63 (12)	1.4763	[15]
13	CH_3	H	H	H	CH_3	CH_3	H	H	70—72 (20)	1.4763	[15]
14	CH_3	CH_3	H	H	CH_3	H	H	H	57—58 (8)	1.4797	[12]
15	CH_3	H	CH_3	CH_3	H	H	H	H	70—72 (19)	1.4747	[12]
16	CH_3	H	CH_3	H	H	H	H	H	65—75 (20)*	1.4766	[15]
17	CH_3	H	H	H	H	H	CH_3	CH_3	68 (17)	1.4818	[15]
18	iso-C_3H_7	H	CH_3	H	H	H	H	H	73—85 (7)	1.4766	[15]
19	t-C_4H_9	CH_3	CH_3	CH_3	H	H	H	H	75—83 (8)	1.4835	[15]
20	H	H	H	H	H	CH_3	CH_3	H	54—64 (10)*	1.4898	[15]
21	CH_3	CH_3	CH_3	H	H	H	CH_3	H	59—70 (13)*	1.4695	[15]
22	CH_3	H	H	H	CH_3	H	H	H	67 (8)*	1.4810	[25]
23	C_2H_5	H	H	H	CH_3	H	H	H	70—74 (12)	1.4845	[25]
24	C_3H_7	H	H	H	CH_3	H	H	H	67—68 (2)	1.4810	[25]
25	CH_3	H	H	H	iso-C_3H_7	H	H	H	81—81 (9)	1.4821	[25]
26	C_3H_7	H	H	H	iso-C_3H_7	H	H	H	80 (1)	1.4806	[25]

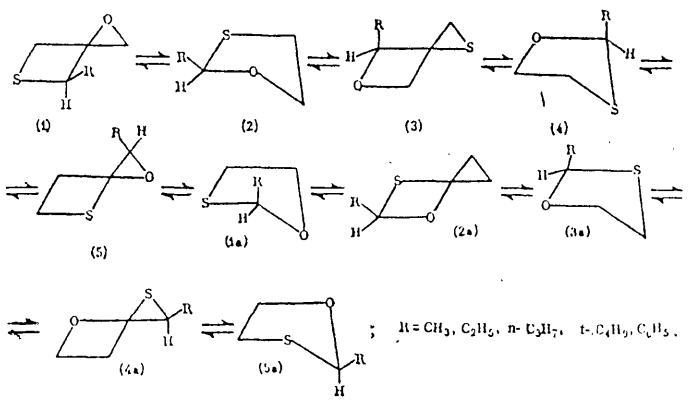
* Mixture of isomers.

1. The Stereochemistry of 1,3-Oxathiolans

The conformational analysis of five-membered rings has developed more slowly, despite their greater abundance in nature, than that of the corresponding six-membered rings. This is a consequence of the conformational mobility of the five-membered rings, for which there is a lower barrier to pseudorotation and a greater number of conformations with similar energies. The stereochemistry of 1,3-oxathiolans has been investigated by ^1H NMR[6,28-42].

It has been concluded[28,32,33] that the most probable conformation of 2-substituted 1,3-oxathiolans is that of a flexible "envelope". There is a possibility of nine different conformations, among which those with O (1 and 1a) or C^5 (2 and 2a) atoms on the "flap" are preferred and agree best with the

observed spin–spin coupling constants:



There is a possibility of the alternative half-chair conformations, where the C(4) or C(5) atoms and one of the heteroatoms lie respectively above and below the plane of the three other atoms; these conformations are in essence energetically equivalent to the corresponding conformations of the "envelope" type[32]. Three main factors determining the conformation of 2-substituted 1,3-oxathiolans have been pointed out[33]. The most important is the decrease of the *trans*-annular van der Waals interactions between the substituents at the C(2) atom and the methylene groups in the 4- and 5-positions. The second important factor is the minimisation of the torsional energies which is achieved when the heteroatom is in the β-position relative to the atom on the "flap" of the "envelope". The third factor is the increase in the size of the groups vibrating about the carbon atom on the "flap". This is attained in oxathiolans having conformations (1) and (2), which has been confirmed by calculations of the free energy change as a function of the changes in the torsional angles[33]. It has been shown that the conformational energy minima for oxathiolan and 2-methyloxathiolan are fairly close. The lowest pseudorotation energy is 12 kJ mol^{-1}.

Thus the conformational behaviour of 2-substituted 1,3-oxathiolans has been investigated in extremely great detail, although it is insufficient for the determination of the overall pattern of the conformational effects. The stereochemistry of 2,4- and 2,5-dialkyl-, 2,4,5-trialkyl-, and 2,4,4,5-tetraalkyl-1,3-oxathiolans has been investigated[6,29–31,37]. It has been confirmed that conformations (1) and (2) are most preferred. Certain thermodynamic constants of the isomeric equilibrium involving substituted 1,3-oxathiolans have also been determined (Table 3); the conformational energies of the alkyl substituents in the 2-position are in the range 5–8 kJ mol^{-1}.[28,36]

Table 3. Thermodynamic constants for the isomeric equilibria involving substituted 1,3-oxathiolans at 25 °C.[29,36]

Equilibrium	$-\Delta H^\circ$, kJ mol^{-1}	ΔS°, J mol^{-1} K	$-\Delta G^\circ$, kJ mol^{-1}
trans-2,5-di-CH_3 ⇄ *cis*-2,5-di-CH_3	4.67	5.65	2.99
trans-C_2H_5-5-CH_3 ⇄ *cis*-2-C_2H_5-5-CH_3	4.87	7.60	2.60
trans-2-iso-C_3H_7-5-CH_3 ⇄ *cis*-2-iso-C_3H_7-5-CH_3	3.03	3.06	2.11
2-C_2H_5-*cis*-2,5-di-CH_3 ⇄ 2-C_2H_5-*trans*-2,5-di-CH_3	1.11	0.21	1.05
2-t-C_4H_5-*cis*-2,5-di-CH_3 ⇄ 2-t-C_4H_9-*trans*-2,5-di-CH_3	—	—	3.99
trans-2,4-di-CH_3 ⇄ *cis*-2,4-di-CH_3	0.18	0.11	0.15

2. Stereochemistry of 1,3-Oxathianes

The structure of 1,3-oxathianes has been studied by ^{1}H NMR and by measuring their dipole moments[10,12,15,16,42–48]. The different bond lengths (1.41 Å for C–O, 1.54 Å for C–C, and 1.82 Å for C–S) and valence angles (110° for O–C–C, 111.7° for C–O–C, and 100° for C–S–C) in 1,3-oxathiane resulting in an unusual geometry of its ring. The "ether" part of the molecule (C^4–O–C^2) is more bent than the "thioether" part (C^6–S–C^2) and the axial valence angles are not rigorously parallel. The non-bonding 1,3-interactions are therefore appreciably weakened[10,12].

The main form of the 1,3-oxathiane ring is the chair conformation, although other conformations are also possible[12,48], the torsional and ring strains in 1,3-oxathianes having a greater influence on the energy parameters of different reactions than in the case of more symmetrical molecules[10,42–48]. Two conformations of the chair type are possible for 1,3-oxathianes[12]:

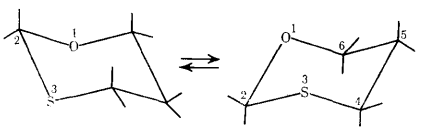


Table 4. Conformational energies* of axial alkyl groups in 1,3-oxathianes, 1,3-dioxanes, and 1,3-dithianes (kJ mol^{-1}).

Alkyl group	Position and orientation				Refs.
	2a	4a	5a	6a	
			1,3-Dioxane		
CH_3	16.65	12.2	3.55—4.1	12.2	[39, 41, 42]
C_2H_5	16.9	—	2.90—3.09	—	[12, 39, 42]
iso-C_3H_7	17.45	—	4.1	—	[12, 39, 42]
			1,3-Oxathiane		
CH_3	13.6	7.4	2.85—3.1	12.3	[12, 43]
C_2H_5	13.6	—	—	—	[12, 43]
iso-C_3H_7	14.85	—	—	—	[12, 43]
			1,3-Dithiane		
CH_3	8.0	6.5	4.9	6.5	[12]
C_2H_5	7.0	—	3.4	—	[12]
iso-C_3H_7	9.7	—	4.4	—	[12]

* The values obtained from data for an acid-catalysed chemical equilibrium.

Table 5. Energies of the 1,3-diaxial interactions (H–CH_3, CH_3–heteroatom) in methyl-substituted 1,3-oxathianes, 1,3-dioxanes, and 1,3-dithianes (kJ mol^{-1})[12,39,42,43].

Compounds	Positions				
	2,4	2,6	4,6	5,4	5,6
1,3-Dioxane	8.5	8.5	3.7	2.0	2.0
1,3-Oxathiane	4.4	9.2	3.4	2.85	—
1,3-Dithiane	4.0	4.0	2.5	2.4	2.4

The free energies of ring inversion in certain *gem*-substituted derivatives are in the range 33.5–48.5 kJ mol^{-1}.[12] These values are quite usual for six-membered rings and are responsible for the ease of inversion close to room temperature. The energy parameters (Tables 4 and 5) show that the energies of the conformational interactions in the 1,3-oxathiane ring are intermediate between those of 1,3-dioxanes and 1,3-dithianes.

As mentioned above, the 1,3-oxathiane molecules exist preferentially in the chair conformation but, owing to the marked ring asymmetry, the chair is distorted and other conformations become possible[48] (Table 6).

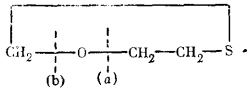
Table 6. Thermodynamic parameters of the chair–"twist" transformations in 1,3-diheterocycloalkanes[48].

Compound	ΔG°, kJ mol^{-1}	ΔH°, kJ mol^{-1}	ΔS°, J mol^{-1} K^{-1}
1,3-Di-t-butylcyolohexane	21.3	25.0	13.4
1,3-Dioxane	33.3	35.9	9.2
1,3-Oxathiane	23.0	25.0	9.2
1,3-Dithiane	7.5	14.2	22.2

Since all four carbon atoms in the 1,3-oxathiane ring are magnetically non-equivalent, these compounds are convenient objects for studies by ^{13}C NMR. The results of ^{13}C NMR measurements for various methyl-substituted 1,3-oxathianes have been reported, the influence of substituents on the chemical shifts of the carbon atom signals have been discussed, and a comparative analysis with 1,3-dioxanes and cyclohexanes has been carried out[55]; the dependence of the influence of the substituents on the nature of the heteroatom has been demonstrated. The chemical shifts for 1,3-oxathianes are in the following ranges: 68–81 p.p.m. for C(2); 23–27 p.p.m. for C(4); 25–42 p.p.m. for C(5); 62–75 p.p.m. for C(6).[55] It has also been shown that the α-effect is very considerable for all the compounds investigated, the equatorial methyl group having a greater deshielding influence than the axial group; this effect is manifested to a greater extent in 1,3-oxathianes than in 1,3-dioxanes and cyclohexanes; the $|\delta|$- and $|j|$-effects are smaller.

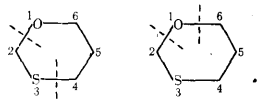
3. The Mass Spectra of 1,3-Oxathiolans and 1,3-Oxathianes

The fragmentation of 1,3-oxathiolans under the influence of electron impact has been investigated[51,52]. It has been found that, among all the possible ring fragmentation pathways, the decompositions (*a*) and (*b*) are the most probable:



It has been concluded that the dominant process (*a*) takes place as a result of the splitting off of an electron from the ring O atom despite the fact that the removal of a non-bonding electron from the S atom requires less energy. In substituted 1,3-oxathiolans the alkyl side group is eliminated from the 2-position more readily than from the 4- and 5-positions. The elimination of an H atom from the 2-, 4-, and 5-position is unlikely[51,52].

The characteristic features of the mass spectra of 1,3-oxathianes are a relatively high intensity of the molecular ion, the absence of metastable transitions, and the preferential shift of the charge to the sulphur-containing fragments[50]. There is a possibility of two main mechanisms of ring opening involving the dissociation of the C^4–S and C^6–O bonds:



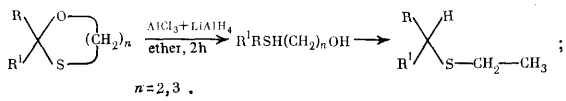
The intensity of the molecular ion peak diminishes with increase of the contribution by the 2-alkyl substituent[50].

IV. THE REACTIONS OF 1,3-OXATHIACYCLOALKANES

The reactions of 1,3-oxathiacycloalkanes have been comparatively little investigated. The heterolytic processes involving the opening of the 1,3-oxathiacycloalkane ring have been studied in greatest detail. Data have been obtained recently on the radical-chain reactions of compounds of this class.

1. Heterolytic Reactions of 1,3-Oxathiacycloalkanes

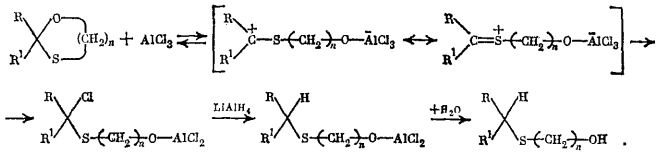
1,3-Oxathiolans and 1,3-oxathianes have been reduced[53,54] with lithium tetrahydroaluminate and aluminium chloride in ether:



$n=2,3$.

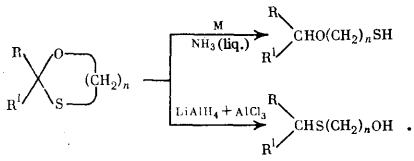
It has been shown that the reductive cleavage involves mainly the C–O bond. Thus the above reaction makes it possible to obtain thioethers from aldehydes and ketones.

On hydrogenolysis with a mixture of $LiAlH_4$ and BF_3 for 2 h, less than 1% of 1,3-oxathiolan reacted, while the $AlCl_3$ + $LiAlH_4$ mixture gives rise under the same conditions to 85–90% of hydrogenation products, mainly the hydroxythioether together with a small amount of a dialkyl sulphide. A mechanism involving the formation of a resonance-stabilised cation in the first stage has been proposed; on reaction with the nucleophilic chloride ion (from $AlCl_3$), this cation gives rise to an α-halogenothioether, which is readily reduced to the thioether[53]:

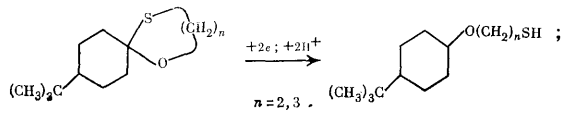


The study of the reductive cleavage of the 1,3-oxathiolan ring with a mixture of lithium tetrahydroaluminate and aluminium chloride or with boron trifluoride in ether[55] confirmed data[53,54] concerning the preferential opening of the 1,3-oxathiolan ring at the C–O bond and not the C–S bond (1,3-dithiolan does not undergo hydrogenolysis). The yields of the reduction products depend greatly on the order of mixing of the reactants. The addition of a Lewis acid to a mixture of oxathiolan and the hydride makes it possible to achieve better yields and to avoid the charring of the products and also permits reduction with the BF_3–$LiAlH_4$ system. The addition of a solution of a 1,3-oxathiacycloalkane to the $AlCl_3$–$LiAlH_4$ or BF_3–$LiAlH_4$ mixture[53,54] results in partial charring of the products in the former case and in the decomposition of $LiAlH_4$ even before it reacts with the oxathiacycloalkane in the latter case[55].

The cleavage of the oxathiacycloalkane ring at the C–S bond can be achieved when 1,3-oxathianes and 1,3-oxathiolans are treated with metals in liquid ammonia. In contrast to the effect of the $LiAlH_4$–$AlCl_3$ mixture, this results in the formation of the corresponding β- or γ-alkoxymercaptans[56–59]:

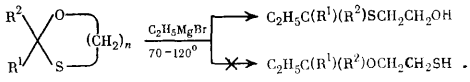


This reaction is widely used in peptide synthesis. Sometimes the reductive cleavage involves both bonds (C–O and C–S), which leads to sulphur-free products. Thus treatment of 2-methyl-2-phenyl-1,3-oxathiolan with sodium in liquid ammonia yields ethylbenzene as the main reaction product[59]. In general 1,3-oxathiolans with the phenyl substituent in the 2-position produce the corresponding alkylbenzenes on reduction[63]. The reduction of various substituted 1,3-oxathiolans and 1,3-oxathianes with metals in liquid ammonia has been studied. It has been shown that the reduction proceeds via the transfer of two electrons and the addition of a proton (from ammonia) to a carbon atom[57]:



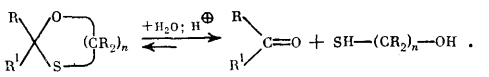
In the reactions of cyclic ketones the yields are 60–90%. For aldehyde derivatives, the yields of alkoxythiols are lower owing to the formation of thiols and olefins in side reactions[57]. The effectiveness of metals in the reduction decreases in the sequence Ca > Li > Na > K. The addition of proton-donating solvents (t-C_4H_9OH, C_2H_5OH) does not increase the yield of the reduction products. In the series of 1,3-oxathianes the yields are higher than for 1,3-oxathiolans.

The cleavage of 1,3-oxathiolans by a Grignard reagent has been investigated[59]:



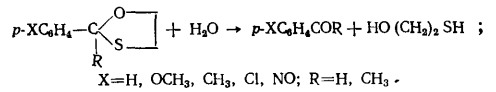
The reaction proceeds with dissociation of the C–O bond, i.e. via the first pathway. The reactivity of 1,3-oxathiolans increases in the sequence 1,3-oxathiolan < 2-ethyl-2-methyl-1,3-oxathiolan ≦ 2-propyl-1,3-oxathiolan ≦ 2-methyl-1,3-oxathiolan. The decrease of reactivity on passing from dioxolans to oxathiolans is associated with the increase of electron density at the C(2) atom[59].

1,3-Oxathiacycloalkanes react with water in the presence of acid catalysts to form the corresponding aldehydes (or ketones) and mercaptoalcohols[60–66]:



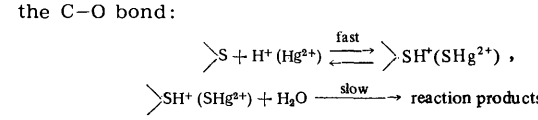
The hydrolysis of 1,3-oxathiolans has been studied in greatest detail, while extremely few data are available for 1,3-oxathianes.

The hydrolysis of 2-aryl-1,3-oxathiolans catalysed by the H_3O^+ and Hg^{2+} ions has been investigated[60]:



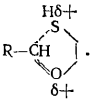
X=H, OCH_3, CH_3, Cl, NO; R=H, CH_3.

It has been shown that 2-aryl-1,3-oxathiolans hydrolyse more slowly than the corresponding 1,3-dioxolans. This has been explained by the fact that oxygen stabilises the α-carbenium ion more effectively than does sulphur[60]. On the basis of the study of the isotope effects and the determination of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for 1,3-oxathiolans relative to 1,3-dioxalans, it was concluded that the acid hydrolysis of 2-phenyl-1,3-oxathiolans proceeds via the $A2$ mechanism with rupture of the C–O bond:



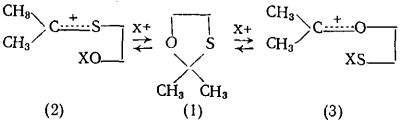
The activation entropies for the hydrolysis of 1,3-oxathiolans are in the range from −17.8 to −24.4 e.u., which is less than the values for 2-phenyl-1,3-oxathiolan (−8.9 e.u.) and 2-methyl-2-phenyl-1,3-dioxolan (−8.9 e.u.), which have been shown to hydrolyse via the $A1$ mechanism and are close to the $\Delta S^{\neq}$ for 4,4,5,5-tetramethyl-2-phenyl-1,3-dioxolan (−14.2 e.u.), which has been shown to involve the $A2$ mechanism. The ratios k_D/k_H for 1,3-oxathiolans are also smaller than the values corresponding to the $A1$ mechanism.

The acid hydrolysis of 2-aryl-1,3-oxathiolans in HCl solutions in water and in a 50:50(%) dioxan–water mixture has been investigated[61]. The study of the isotope effect of the solvent and also the comparative analysis of 1,3-oxathiolans and 1,3-dioxolans led to the conclusion that the hydrolysis proceeds via the $A1$ mechanism with dissociation of the C–S bond and the formation of the intermediate ion:



The isotope effect of the solvent ($k_D/k_H < 2$) is smaller than that usually observed for the $A1$ mechanism ($k_D/k_H > 2$). The low isotope effect of the solvent may be a result of the more intense protonation of the sulphur atom than the oxygen atom and this can be accounted for in its turn by the difference between the S–H and O–H bond lengths[61]. These conclusions have been confirmed by the comparative analysis of oxathiolans and the thioacetals $C_6H_5CH(OCH_3)SC_6H_4R$.[62]

The ^1H NMR study of 1,3-oxathiolans in a solution of the 1:1 FSO_3H + SbF_5 mixture in liquid SO_2 at −60 °C showed[63,64] that protonation leads mainly to the cation (2)(X=H), while the formation of the cation (3) (X=H) is unlikely:



(2) (1) (3)

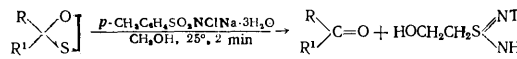
These results have been confirmed by the ^1H NMR study of 2,2-dimethyl-1,3-dithiolan under the same conditions. It was concluded that the hydrolysis of 1,3-oxathiolans proceeds with the dissociation of the C–O bond via the $A1$ mechanism. The preferential dissociation of the C–O bond on protonation and on formation of compound (6) in the kinetic stage can be explained mainly by the lower basicity of the S atom in relation to the proton compared with the O atom. It has been suggested that the intermediate product is formed without the participation of the nucleophile. The opening of the 1,3-oxathiolan rings on bromination has also been investigated[63,64]. It was shown that the basicity factor does not play here a major role and that in this instance there is a possibility of the dissociation of the C–O and C–S bonds with formation of the corresponding ions (6)(X=Br) and (7)(X=Br).

The study of the hydrolysis of 1,3-oxathiolan, 2-methyl-1,3-oxathiolan, and 2,2-dimethyloxathiolan in aqueous solutions of $HClO_4$ and $DClO_4$ showed[65] that the rate of reaction depends on the substituents in the 2-position. For 2-methyl-1,3-oxathiolan, it is approximately 2250 times higher than for the unsubstituted 1,3-oxathiolan and for 2,2-dimethyl-1,3-oxathiolan is 57 times higher than for 2-methyl-1,3-oxathiolan[71]. It is believed[65] that the hydrolysis proceeds via the *A*1 mechanism with dissociation of the C–O bond.

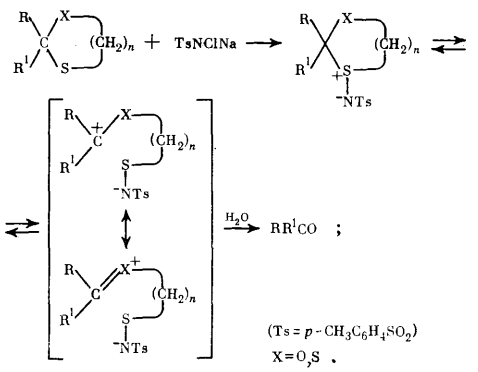
It is seen from the data considered that the mechanism of the hydrolysis of 1,3-oxathiolan has still not been determined unambiguously.

The hydrolysis of 2-substituted 1,3-oxathianes by $HClO_4$ in a H_2O/D_2O mixture has been studied[66] and it has been found that the relative rates of the acid hydrolysis of 1,3-oxathianes, 2-methyl-1,3-oxathiane, and 2,2-dimethyl-1,3-oxathiane are 1, 45, and 8×10^6 respectively. The rate of hydrolysis of 2-methyl-1,3-oxathiane proved to be much lower than was assumed. This can be explained by the fact that only the isomer with the axial conformation is hydrolysed; if account is taken of the mole fraction of the axial conformation, then the rate of hydrolysis of 2-methyl-1,3-oxathiane increases approximately by a factor of 300.[66] The hydrolysis of 1,3-oxathiacycloalkanes makes it possible to synthesise various aldehydes or ketones or to regenerate them when thioacetal or thioketal protecting groups are used.

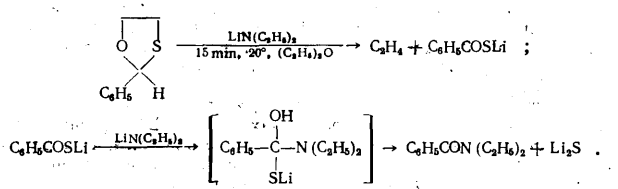
A convenient and rapid method of regenerating ketones and aldehydes by treating 1,3-oxathiacycloalkanes with chloramine T has been proposed[67,68]:



The reaction proceeds under mild conditions, the yields reaching 90–100%. Apart from the carbonyl compound, 2-hydroxyethyltoluene-p-sulphonimidosulphine-toluene-p-sulphonylimine and bis(2-hydroxyethyl) disulphide are formed (the latter product is obtained when less than 2 moles of chloramine T per mole of the oxathiolan are used in the reaction). The intermediate formation of a carboxonium ion has been postulated:

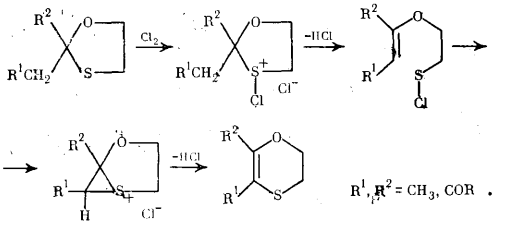


Olefins which are difficult to obtain by other methods can be synthesised by treating 1,3-oxathiacycloalkanes with alkaline reagents, for example, lithium dialkylamides. The reaction of 2-phenyl-1,3-oxathiolan with lithium diethylamide in ether has been studied in detail[69]:



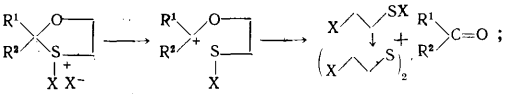
The yields of the olefins were nearly quantitative. Olefins can be obtained analogously also from the more readily available 1,3-dioxolans. However, olefins which are difficult to obtain, such as *trans*-cyclo-octene, *cis*- and *trans*-cyclo-octa-1,5-dienes, and also tetrasubstituted olefins can be synthesised more conveniently from 1,3-oxathiolans[69–71].

The chlorination of 1,3-oxathiolans having α-methylene groups leads to 5,6-dihydro-1,4-oxathi-ines[72–75]:

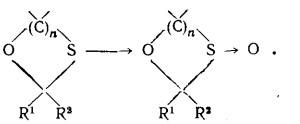


The reaction is carried out at low temperatures (between −20° and −70 °C) and the yields are 55–60%.

In the absence of α-methylene group, *C*-halogenation takes place instead. For example, the chlorination and bromination of certain substituted 1,3-oxathiolans lead to the formation of the corresponding ketones and disulphides[75]:



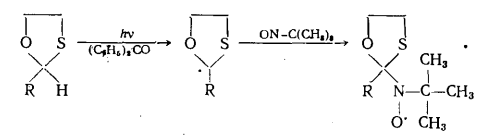
The oxidation of 1,3-oxathianes[75] and 1,3-oxathiolans[77,78] constitutes the main method of synthesis of cyclic sulphoxides:



The study of the oxidation of 1,3-dithiane and 1,3-oxathiane[76] showed that the content of isomers with an axial or equatorial SO group depends both on the cyclic sulphide being oxidised and on the oxidant. The content of the 1,3-oxathiane isomer with an axial SO group increases in the following sequence of oxidants: t-BuOCl > $NaIO_4$ > H_2O_2 > N_2O_4.

2. Homolytic Reactions of 1,3-Oxathiacycloalkanes and 1,3-Dithiacycloalkanes

When 1,3-oxathiacycloalkanes and 1,3-dithiacycloalkanes interact with sources of free radicals, the abstraction of hydrogen atoms results in the formation of 1,3-diheterocycloalkyl radicals. Thus the benzophenone-sensitised ultraviolet irradiation of 1,3-oxathiolans leads to the formation of 1,3-oxathia-2-cyclopentyl radicals, which in the presence of a spin-trapping agent (2-methyl-2-nitrosopropane) yield fairly stable spin-adducts (nitroxy-radicals) whose signals have been detected in the EPR spectra[79–82]:

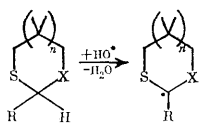


Nitroxy-radicals containing 1,3-oxathia- and 1,3-dithia-2-cycloalkyl residues are formed on photolytic decomposition of t-butyl peroxide in 1,3-diheterocycloalkanes in the presence of 2-methyl-2-nitrosopropane[80–82]. The spectroscopic

characteristics of the nitroxy-radicals containing the 1,3-diheterocycloalkane residue show that the formation of radicals with an unpaired electron at the ring C(2) atom is the dominant process[79-82]. Consequently, under the conditions investigated (20–25 °C), the *t*-butoxy-radicals arising on photolysis of t-butyl peroxide attack very selectively the carbon–hydrogen bonds located between the two heteroatoms.

The increase of the hyperfine coupling constant a_n on passing from 1,3-dioxacycloalkane to 1,3-oxathia- and 1,3-dithia-cycloalkanes is evidently associated with the increase of electron density at the N atom of the nitroxy-group as a consequence of the decrease of the negative inductive effect following the replacement of the ring oxygen atoms by the less electronegative sulphur atoms[79-82]. In all the examples investigated the EPR spectra did not reveal signals due to nitroxy-radicals which might have been formed from the acyclic acylheteroalkyl radicals. This shows that the 1,3-oxathiacycloalkyl radicals do not undergo a rearrangement under the conditions investigated[79-82].

The structure of the radicals arising from 1,3-oxathia- and 1,3-dithiacycloalkanes under the influence of hydroxy- and t-butoxy-radicals has been studied directly[82,83,86-89]. When the hydroxy-radicals generated by the reaction Ti(III) + H_2O_2 → Ti(IV) + HO^- + $\dot{O}H$ react with 1,3-oxathia- and 1,3-dithiacycloalkanes in water at 25 °C, 1,3-dihetero-2-cycloalkyl radicals are formed more selectively (Table 7)[82,83,87], in contrast to 1,3-dioxacycloalkanes[84,85]:



n = 0, 1; X = O, S; R = H, CH_3, n-C_3H_7, $CH(CH_3)_2$.

Under the same conditions, cyclic acetals give rise to di- and mono-alkoxycycloalkyl radicals[82,84,85]. The replacement of the oxygen atom by the sulphur atom either greatly activates the hydrogen atom adjoining the two heteroatoms or increases the lifetime of the 1,3-dihetero-2-cycloalkyl radicals formed compared with other types of radicals.

An analogous picture has been observed in the interaction of sulphur-containing 1,3-oxaheterocycloalkanes with t-butoxy-radicals[89]. In the analysis of the EPR spectra and in the study of the configurations of sulphur-containing 1,3-dihetero-2-cycloalkyl radicals in combination with calculations by quantum-chemical methods[86-89], it was established that the sulphur atom exhibits a fairly large delocalising effect (~ 19% of the spin density) and flattens the pyramidal structure of the paramagnetic centre, which is characteristic of 1,3-dioxa-2-cycloalkyl radicals[85,90].

Thus the configuration of the tervalent carbon atom is flattened on passing from 1,3-dioxa-2-cycloalkyl radicals, via 1,3-oxathia-2-cycloalkyl radicals, to 1,3-dithia-2-cycloalkyl radicals.

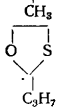
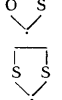
1,3-Oxathia- and 1,3-dithia-cycloalkanes are extremely active donors of a hydrogen atom in the reaction with t-butoxy-radicals. The activities of 1,3-diheterocycloalkanes in the reaction involving the abstraction of a hydrogen atom by t-butoxy-radicals have been determined by the method of competing reactions[82,91,92]:

$$[(CH_3)_3CO]_2 \rightarrow 2(CH_3)_3CO^{\cdot};$$

$$(CH_3)_3CO^{\cdot} \begin{cases} \xrightarrow[+RH]{k_a} (CH_3)_3COH + R^{\cdot} \\ \xrightarrow{k_d} CH_3COCH_3 + CH_3^{\cdot} \end{cases}.$$

At a constant temperature the parameter k_a/k_d is a measure of the reactivity of 1,3-diheterocycloalkanes in the abstraction of a hydrogen atom by t-butoxy-radicals. At 130 °C the ratio k_a/k_d is 5.0–8.0 litre mol^{-1} for 1,3-oxathiacycloalkanes and 7.0–10.0 litre $mole^{-1}$ for the corresponding dithia-derivatives[82,91,92].

Table 7. EPR parameters of the radicals generated from 1,3-oxathia- and 1,3-dithia-cycloalkanes by treatment with hydroxy-radicals in water[79,83,87].

Radical	HFI constant, G			*g*-Factor
	$a_{\alpha\text{-H}}$	$a_{\beta\text{-H}}$	$a_{\gamma\text{-H}}$	
	—	16.6 (q)	0.5 (m)	2.0037
	—	15.5 (t)	0.5 (m)	2.0037
	—	15.2 (d)	0.5 (m)	2.0037
	—	17.7 (q)	0.5 (m)	2.0047
	—	9.0 (t)	0.5 (m)	2.0077
	5.1 (d)	—	1.1 (m)	2.0051
	14.4 (d)	—	1.0 (m)	2.0039
	13.5 (d)	—	1.3 (m)	2.0050
	15.2 (d)	—	1.5 (m)	2.0054

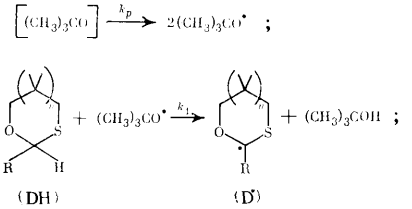
The increase of the reactivity of 1,3-diheterocycloalkanes as the oxygen atoms are substituted by sulphur atoms is common to five-, six-, and seven-membered rings. There is a greater increase of activity on passing from 1,3-dioxacycloalkanes to 1,3-oxathiacycloalkanes than on passing from 1,3-oxathiacycloalkanes to 1,3-dithiacycloalkanes. The alkyl substituents in 1,3-diheteroanalogues of cycloalkanes have little influence on their reactivity. The partial rate constants for the OCH(R)S and SCH(R)S (R = CH, n-C_3H_7, or iso-C_3H_7) fragments found by an additive scheme[92] are in the ranges $(k_a/k_d)^{130^\circ}_{OCH(R)S}$ = 5.3–8.2 litre mol^{-1} and $(k_a/k_d)_{SCH(R)S}$ = 6.3–9.6 litre mol^{-1} for heterocycles with different numbers of carbon atoms in the ring.

The partial contributions of the OCH(R)S and SCH(R)S groups are more than 80% of the effective rate constant and the hydrogen atom is therefore mainly abstracted at 130 °C from the carbon atom adjoining the two heteroatoms[82,92]. It

is striking that the following dependence of the reactivity on ring size is common to the oxygen- and sulphur-containing 1,3-diheterocycloalkanes: 1,3-diheterocyclohexanes < 1,3-diheterocycloheptanes < 1,3-diheterocyclopentanes[92].

The results have been interpreted[82,91,92] within the framework of ideas concerning the polar effects in the homolytic abstraction of a hydrogen atom by free radicals. Evidently the higher reactivity of 1,3-oxathia- and 1,3-dithia-cycloalkanes compared with that of 1,3-dioxacycloalkanes is due to a more favourable combination of polar factors in the transition state of the reaction involving the abstraction of a hydrogen atom by the electrophilic radical $(CH_3)_3CO^{\bullet}$[82,91,92].

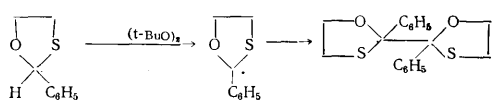
In the reaction initiated by t-butyl peroxide, 1,3-oxathiacycloalkanes are converted at 120–150 °C into esters of thiolocarboxylic acids[82,93]. The initial rate of formation of the thioesters varies linearly with the substrate concentration and is directly proportional to the square root of the initiator concentration[82,93], which suggested a radical-chain unbranched mechanism of the isomerisation of 1,3-oxathiacycloalkanes with quadratic chain termination by the rearranged radicals (A·):



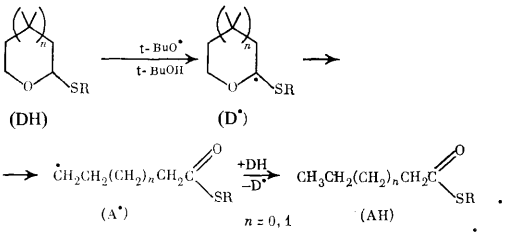
The rate-limiting stage of the reaction is the abstraction of a hydrogen atom from the substrate by the rearranged radical A·. The values of the kinetic parameter $(k_3/\sqrt{k_4})^{130^\circ}$ found, which are a measure of the reactivity of 1,3-oxathiacycloalkanes in the free radical isomerisation reaction, have shown[82,89] that 1,3-oxathiacycloalkanes are 2–3 times less reactive than 1,3-dioxacycloalkanes[82,93]. This was confirmed by the method of competing reactions[94].

The reduced reactivity of 1,3-oxathiacycloalkanes in the free radical isomerisation reaction compared with 1,3-dioxacycloalkanes is in direct contrast with their higher reactivity in the abstraction of a hydrogen atom by t-butoxy-radicals and is evidently associated with the less favourable combination of polar factors in the stage involving the abstraction of a hydrogen atom by the relatively nucleophilic carbon-centred acylheteroalkyl radical A· in the case where the ring contains a sulphur atom, which is less electronegative than oxygen.

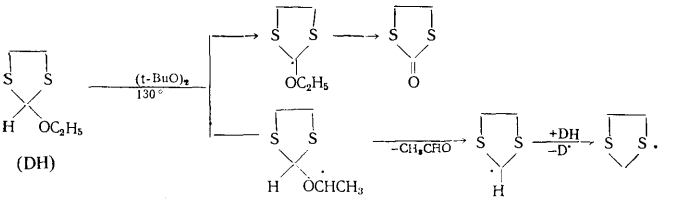
If the 1,3-oxathia-2-cycloalkyl radicals formed are fairly stable and do not undergo a unimolecular rearrangement, they recombine with formation of the corresponding dimeric product. Thus the reaction of 2-phenyl-1,3-oxathiolan with t-butyl peroxide at 130 °C results in the formation of a mixture of the *threo*- and *erythro*-isomers of bis-2-phenyl-1,3-oxathiolan[96]:



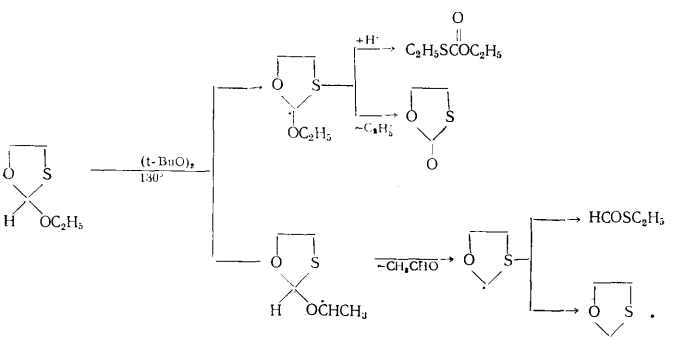
2-Alkylthiotetrahydropyrans and 2-alkylthiotetrahydrofurans isomerise analogously to 1,3-dithiolan[97–100]:



The reaction involving 2-ethoxy-1,3-dithiolan, in which only the cleavage products, namely ethylene dithiocarbonate and 1,3-dithiolan, are formed is somewhat more complex[101]:

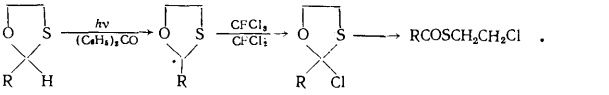


It has been suggested that the former product is formed via the 2-ethoxy-1,3-dithia-2-cyclopentyl radical and that the latter product arises as a result of the abstraction of a hydrogen atom from the α-position in the ethoxy-group via a stage involving the formation and fragmentation of the α-1,3-dithiacyclopentyl-2-hydroxyethyl radical[101]. Isomerisation and cleavage products are formed simultaneously from 2-ethoxy-1,3-oxathiolan[102]:



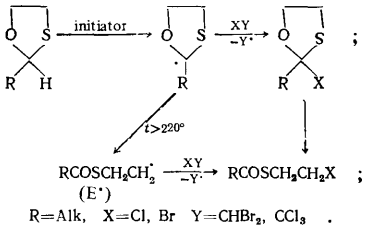
Linear and cyclic thiocarbonates are formed via the 2-ethoxy-1,3-oxathia-2-cyclopentyl radical and 1,3-oxathiolan and ethyl thioformate are formed via the 1,3-oxathiacyclopentyl-2-hydroxyethyl radical arising as a result of the abstraction of a hydrogen atom from the α-position in the ethoxy-group[102].

In polyhalogenomethanes in the presence of free-radical initiators, 1,3-oxathiolans are selectively converted into halogenothioethers, which has been attributed to the involvement of the solvent in the chain propagation stage[79,97–99]. Thus the photolysis of 2-alkyl-1,3-oxathiolans in $CFCl_3$ in the presence of benzophenone results in the formation of chloroethyl esters of thiolocarboxylic acids probably via the corresponding cyclic chlorides, which are unimolecularly converted into chlorothioethers under the reaction conditions:

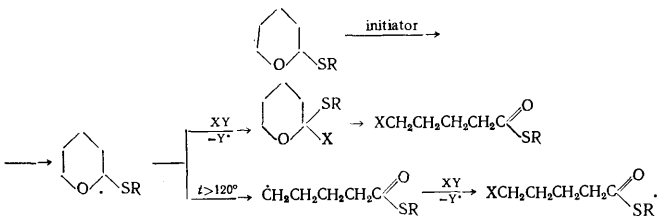


In the reaction initiated by lauroyl peroxide (at 80 °C) or

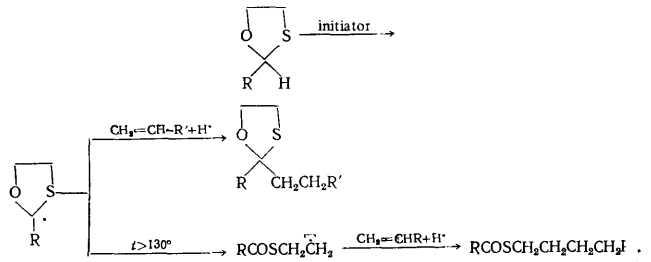
t-butyl peroxide (at 120–150 °C) in polyhalogenomethanes (CCl_4, CCl_3Br, and $CHBr_3$) 1,3-oxathiolans are converted into chloro- and bromo-thioethers[98,99]



The authors[98,99] do not rule out the possibility of the formation of halogenothioethers at relatively high temperatures (> 120 °C) via a stage in which a halogen atom is obstructed by the rearranged acylthioethyl radical E·. Under analogous conditions (80–150 °C), 2-alkylthiotetrahydropyrans give rise to esters of δ-halogenothiolovaleric acids[99], whose formation can be represented as proceeding both via a cyclic halogeno-derivative and via a stage in which a halogen atom is obstructed by the rearranged radical E·:



On interaction with terminal olefins in the presence of radical initiators, 1,3-oxathiolans yield 2-alkyl-1,3-oxathiolans and alkyl thioacylates, whose formation is regarded as proceeding via a stage in which the 1,3-oxathia-2-cyclopentyl and the isomeric acylthioethyl radicals add to the double bond of the olefin[99]:



At relatively low temperatures (≤ 70°) only 2-alkyl-1,3-oxathiolans are formed[99]

---oOo---

On the basis of the data considered, one may reach definite conclusions concerning the methods of synthesis, structure, and types of reactions of 1,3-oxathiacycloalkanes.

The general and most effective methods of synthesis of 1,3-oxathiacycloalkanes involve acid-catalysed reactions of mercaptoalkanols with aldehydes, ketones, alkyl vinyl ethers, and orthoesters.

The main conformation of 1,3-oxathiolans is that of an inverted envelope. The 1,3-oxathiane ring exists preferentially in the chair conformation but the asymmetry of the ring gives rise to an increased probability of other conformations compared with 1,3-dioxanes.

The majority of the heterolytic reactions of 1,3-oxathiocycloalkanes proceed with the opening of the ring at the C–O or C–S bonds. Five-membered 1,3-oxathiacycloalkanes are the most reactive.

The high reactivity of the hydrogen atoms at the carbon atom linked to the two heteroatoms is responsible for the high selectivity of the attack by free radicals on the 2-position in the heterocycle. The mode of the homolytic reactions of substituted 1,3-oxathiacycloalkanes is therefore determined mainly by the rate of formation of the 1,3-oxathia-2-cycloalkyl radicals and the ability of the latter to participate in a unimolecular rearrangement with formation of a thioester, in addition to carbon–carbon double bonds, or in the abstraction of a halogen from polyhalogenoalkanes.

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The Reactivity of 1,3,2-Diheterophospholans Containing a Tricoordinate Phosphorus Atom

M.A.Pudovik, V.V.Ovchinnikov, R.A.Cherkasov, and A.N.Pudovik

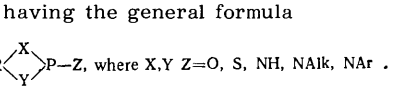
The results of studies on the reactivity of 1,3,2-di-heterophosphacycloalkanes containing a tricoordinate phosphorus atom carried out in recent years are examined and surveyed. Muchattention has been devoted to reactions leading to an increase of the coordination number of the ring phosphorus atom and also to exocyclic and endocyclic substitution reactions. The mechanisms and certain stereochemical characteristics of the reactions of cyclic phosphorus compounds are discussed. In a few instances the reactivities have been estimated quantitatively.
The bibliography includes 245 references.

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I. INTRODUCTION

The characteristic features of the reactivity of cyclic compounds of tricoordinate phosphorus were noted previously in a review[1,2]. During the time which has elapsed since then, new interesting data have accumulated, supplementing and deepening the available information about the mechanisms of reactions of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes having the general formula



The description of these reactions is based on ideas about the structures of the intermediates or transition states involving an increase of the coordination number of the phosphorus atom. In many cases the reactivity of these compounds is explained from the standpoint of ring strain. Such inferences are based on the data accumulated hitherto on the cyclic phosphorus compounds: the steric structure of the ring itself and of the exocyclic substituent linked to it, the distribution of electron density in the molecule, the electronic situation at the phosphorus nucleus itself—the character of the hybridisation of its lone electron pair (LEP), and the strength of the phosphorus–heteroatom bond.

The steric structures of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes with a tervalent phosphorus atom have been studied in detail by various methods[3-5]. An important feature of the structure of five-membered phosphorus rings compared with the phosphorinane and acyclic analogues is a significantly reduced (93–100°) endocyclic X–P–Y angle. As a consequence of this, the electron density at the centre of the triad is reduced, which is clearly manifested by the deshielding of the phosphorus nucleus, according to ^{31}P NMR data, with decrease of ring size[6]. At the same time the LEP of phosphorus in such compounds has a reduced *p* character compared with the six-membered and acyclic derivatives with similar structures[7] and is therefore less reactive with respect to electrophiles. This factor is responsible for certain specific features of the reactivity of diheterophospholans. Many aspects of a purely synthetic type are not considered in this review. We thought it useful to deduce and as far as possible survey the characteristics of the reactivity of 1,3,2-diheterophosphacycloalkanes with a tervalent phosphorus atom, particular attention being devoted to compounds with a five-membered ring.

II. BASICITY AND COMPLEX FORMATION

Data concerning the ability of phosphorus-containing heterocycles to participate in nucleophilic reactions can be obtained from the analysis of the results of studies of the protonation of these compounds and of their tendency to form metal complexes.

It is known[8] that the introduction of electron-accepting substituents at a tricoordinate phosphorus atom reduces significantly the electron density at this atom, which entails a decrease of nucleophilic reactivity. An analogous effect is observed when phosphorus is incorporated in a ring. Thus the observed high ionisation potential of 1,3-butylene phosphorochloridite (9.90 eV) compared with diethyl phosphorochloridite (9.51 eV) may indicate a weakening of the interaction of the LEP of the phosphorus and oxygen atoms ($n_P - n_O$) on cyclisation[9]. In this respect, the absence of interaction between HCl and five-membered cyclic phosphorochloridites, obtained by the reaction

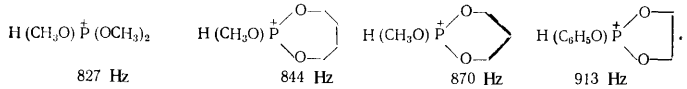


is also striking[10].

Acyclic and cyclic six-membered phosphorochloridites as well as 1,3,2-oxaza- or 1,3,2-diaza-phospholans are obtained only in the presence of hydrogen chloride acceptors[10]. While gaseous HCl does not interact with 2-chloro-1,3,2-dioxaphospholans, on replacement of the chlorine atom by an alkoxy-, alkyl, or dialkyl-amide group the tervalent phosphorus atom can be protonated[11].

An important characteristic of the protonated phosphite is the constant $^1J_{PH}$, which is extremely sensitive to a change in the electronic and steric environment of phosphorus. The

increase of $^1J_{PH}$ on passing from acyclic to six- and five-membered cyclic as well as bicyclic protonated phosphites is consistent with the increase of the s character of the LEP of the phosphorus atom in the initial compounds[11,12]:

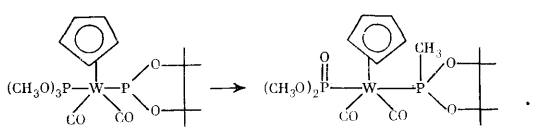


The results of the determination of the proton affinities and ionisation potentials of cyclic phosphites in the gas phase[13] also confirm the earlier conclusion that the basicity of the phosphorus atom decreases in the following sequence of phosphites: acyclic > six-membered > five-membered > bicyclic[14,15], which is associated with the increase of the ring strain in this sequence.

It has been suggested that the repulsion between the LEP of the oxygen and phosphorus atoms increases the energy of the highest occupied molecular orbital of the unshared electron pair of the phosphorus atom in an acyclic phosphite and its proton affinity. The inclusion of a phosphorus(III) atom in a five-membered ring alters the geometry of the pyramidal structure of the phosphorus atom and leads to strain in the cyclic system. As a consequence of this, the degree of hybridisation of the LEP in the ring phosphorus and oxygen atoms changes, their mutual repulsion diminishes, and the protophilic properties of the cyclic phosphite are diminished[13].

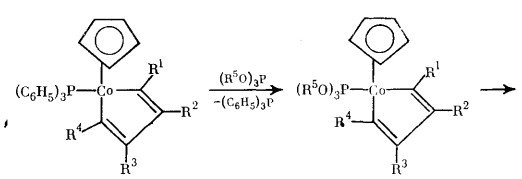
By virtue of the low basicity of phosphorus in dioxaphospholans, 1,2-phenylenephosphophosphorous acid exists in the condensed phase in a form with a tricoordinate phosphorus atom[16]. The presence of a small amount of a similar structure has been noted for the oxathiaphospholan analogue[17]; six-membered cyclic and acyclic diorganylphosphorous acids exist mainly as hydrophosphoryl derivatives $(RO)_2P(O)H$.

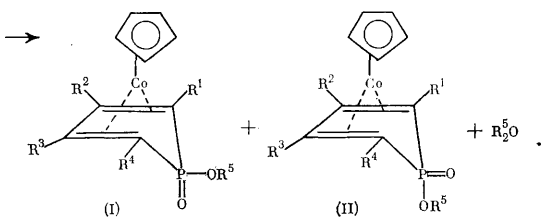
The reduced electron-donating capacity of the LEP of phosphorus in cyclic phosphites is also indicated by data demonstrating a lower stability of their complexes with phenols[18], BH_3, BF_3, and metals[19-21]. It is significant that the basicity of the phosphorus atom in phosphorinane structures and hence the stability of the adducts with BH_3 depend on the steric orientation of the LEP. Thus the equatorial electron pair in six-membered cyclic phosphites is less "basic" than the axial pair[9]. However, the formation of complexes of these compounds with Lewis acids leads to adducts in which the complex-forming agent is in the equatorial and apparently less sterically hindered position[20]. The cyclic phosphites in complexes can undergo intramolecular alkylation[22]:



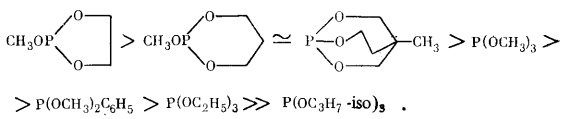
The isomerisation of coordinated phosphites has been noted in substitution reactions proceeding via Scheme 1:[23]

Scheme 1





The use of cyclic phosphites in this reaction showed that at the triphenylphosphine substitution stage the rate of the process is independent of the nature of the phosphite. However, at the stage involving isomerisation of the phosphacyclopentadienyl derivatives (I) and (II) within the complex, the following phosphite activity series was found:

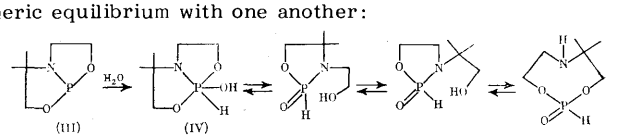


The above sequence can be explained by taking into account the fact that the isomerisation process proceeds via a transition stage with phosphorus(V),[23] in which there is a significant decrease of ring strain in cyclic phosphites. The small steric effect of cyclic dihydroxyalkylene groups compared with alkoxy-groups (particularly with an iso-structure)[23,24] also facilitates the reaction.

III. REACTIONS WITH COMPOUNDS CONTAINING A MOBILE HYDROGEN ATOM

1. Water, Alcohols, and Phenols

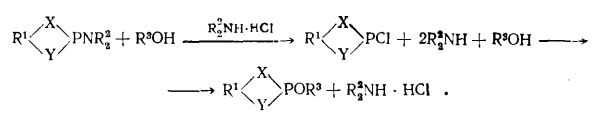
The interaction of cyclic phosphites with water and aqueous organic solvents is used widely as a convenient method of synthesis of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes containing the hydrophosphoryl group[25]. Dioxaphospholans[26,27] and oxazaphospholans[28] unsubstituted in the ring hydrolyse as a rule with ring opening, the hydrolysis being significantly accelerated by acid catalysts[29]. The presence of alkyl substituents at endocyclic carbon atoms greatly stabilises the cyclic fragment and hydrolysis takes place with retention of the ring[29-31]. In the low-temperature hydrolysis of condensed phosphoramidites (III),[32,33] the formation of the hydroxyphosphoranes (IV) was detected by ^{31}P NMR. These compounds are transformed further into derivatives of tetracoordinate phosphorus involved in a tautomeric equilibrium with one another:



The reactions of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes with alcohols, phenols, and glycols lead either to exocyclic substitution[34-41] or to the dissociation of one or both endocyclic phosphorus–heteroatom bonds[42-51]. There is also a possibility of the formation of monocyclic phosphoranes or spirophosphoranes with a P–H bond[52-55]; in many instances the reaction products are compounds of hexacoordinate phosphorus[56-59].

The study of the reactions of the amides of cyclic phosphorus acids with proton-donating reagents established the important role of acid catalysis[38,60-62]. Thus alcoholysis of phosphoramidites is accelerated by amine hydrochlorides,

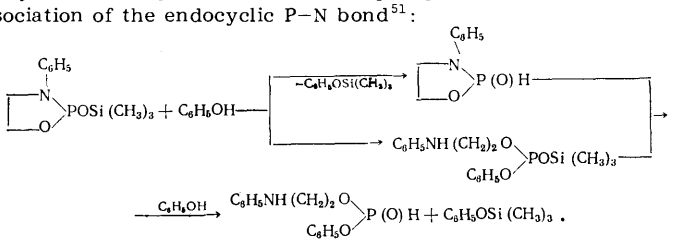
usually present as admixtures in the initial compound. This is accompanied by the intermediate formation of tervalent phosphorus chlorides which are readily esterified with regeneration of the catalyst[62]:



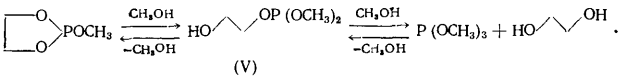
The acceleration of reactions of this type under the conditions of base catalysis has been noted[63].

The rates of the reactions of 2-dimethylamino-1,3,2-dioxaphospholan with phenol, butanol, and t-butyl alcohol in benzene increase with increase of the acidity of the hydroxylated reagent[38]. The reactivity of five-membered cyclic phosphoramidites in a non-catalysed reaction with butanol is significantly higher than that of the corresponding acyclic derivatives[38]; an increase of the number of alkyl substituents in the ring increases the reactivity of cyclic phosphoramidites in these reactions. The interpretation of the results is fairly difficult, particularly since it has been shown by kinetic studies[41] that the first stage of the alcoholysis involves complex formation between the alcohol and the phosphoramidite. According to the authors[41], this hinders comparison of the kinetic parameters of the reaction with the structures of the initial reactants.

The alcoholysis of 1,3,2-oxazaphospholans containing the exocyclic POSi group takes place simultaneously via two pathways—the desilylation of the initial phosphoramidite and dissociation of the endocyclic P–N bond[51]:

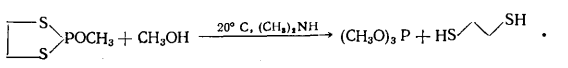


The P–N, P–O, and P–S bond strengths in 1,3,2-diheterophospholans unsubstituted in the carbon component of the ring and also the relative contributions of the *exo*- and *endo*-pathways of the methanolysis depend on different factors and in the first place on the temperature and acidity of the reaction medium and on the basic additives[47,48]. The methanolysis of 2-methoxy-1,3,2-dioxaphospholan does not take place in an alkaline medium; in the absence of bases, equilibrium involving the formation of the intermediate (V) with an open-chain structure has been noted[48]:

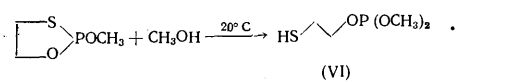


(V)

At 20 °C methanol does not interact with 2-methoxy-1,3,2-dithiaphospholan; the P–O bond is cleaved only at 80 °C in the presence of an excess of methanol. However, after the addition of catalytic amounts of dimethylamine, both P–S bonds of the heterocycle are readily ruptured even at room temperature[47]:

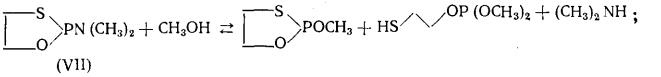


The use of oxathiaphospholan leads to the formation of β-mercaptoethyl dimethyl phosphite(VI):

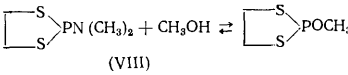


(VI)

The methanolysis of 2-dimethylamino-1,3,2-oxathia- and 2-dimethylamino-1,3,2-dithia-phospholans (VII) and (VIII) in the absence of basic additives is reversible[47]:

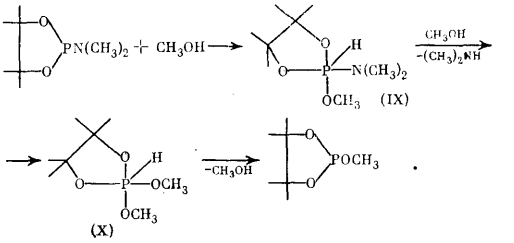


(VII)



(VIII)

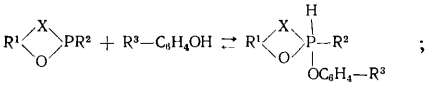
An increasing amount of data confirming that the alcoholysis of 1,3,2-diheterophospholans by alcohols and phenols involves the intermediate formation of structures of the phosphorane type with a P–H bond has been published recently[35,39,52–55]. The formation of the pentacoordinate intermediates (IX) and (X) in the reaction of 2-dimethylamino-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan with methanol has been detected by ^{31}P NMR:[36]



(IX)

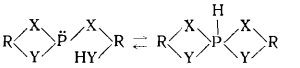
(X)

1,3,2-Dioxa- and 1,3,2-oxaza-phospholans react with substituted phenols also to form addition products which contain a pentacovalent phosphorus atom and are in equilibrium with the initial reactants[53,64]:



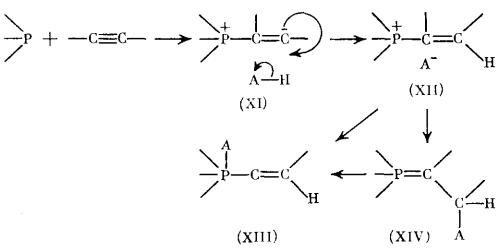
R^1=*o*-C_6H_4—, —$C(CH_3)_2C(CH_3)_2$—; R^2=Alk, Ar; R^3=*p*-NO_2, *p*-Cl, H, *p*-NH_2, *o*-NH_2; X=O, NH.

The formation of a phosphorane is favoured by a decrease of the temperature of the reaction mixture and an increase of the acidity of the phenol. It is believed[53] that the rate-determining stage in these reactions is the protonation of the phosphorus atom. An intramolecular version of such addition has been discovered in the case of 1,3,2-diheterophospholans containing functional groups with a mobile hydrogen atom in the β-position in the exocyclic substituent:



The position of this tautomeric equilibrium depends on the temperature, the nature of the solvent, the heteroatoms in the ring, and the nature of the substituents in the latter. Data on this question have been exhaustively described in a number of communications[65–71], although one should note that the thermodynamic characteristics of such processes, like those of many reactions of 1,3,2-diheterophosphacycloalkanes with proton donors, have not been described in the literature.

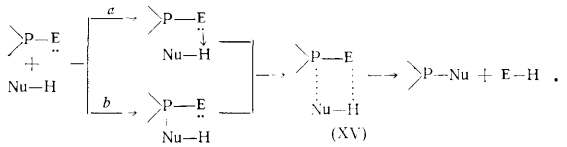
The course of the reactions of cyclic phosphites with alcohols in the presence of a third reactant—a compound with a C=C bond, was unexpected[54]:



(XI) (XII) (XIII) (XIV)

The dipolar ion (XI) formed in the first stage interacts with the proton-donating reactant A–H, leading to the phosphonium intermediate (XII) which is stabilised by being converted into the final phosphorane (XIII) either directly or via the unstable ylide (XIV).

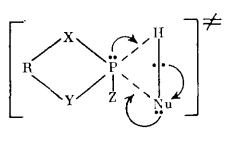
The available experimental data do not allow a single mechanism to be postulated for the interaction of 1,3,2-diheterophosphacycloalkanes with water, alcohols, and phenols. A number of workers have expressed the view that the substitution of an exocyclic group is an S_N2 process [with respect to phosphorus(III)] in which the reactivity of cyclic organophosphorus compounds depends on the ratio of the electronic and steric characteristics of the exchanging groups and also on the nature of the ring heteroatoms[61]. If the exocyclic substituent at the tervalent phosphorus atom is a group which is difficult to eliminate but is fairly basic, there is a possibility of electrophilic cooperation as a result of preliminary protonation (pathway *a*) or protonation after orientation of the nucleophile (pathway *b*):



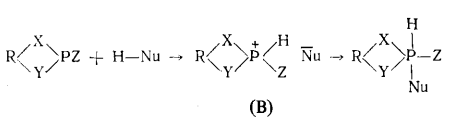
(XV)

According to Mathis[37], these reactions can proceed via a four-centre cyclic transition (XV) or via the formation of the intermediate (XV) having a similar structure. Such association can take place also with participation of an endocyclic heteroatom[47], whereupon substitution occurs with ring opening.

On the other hand, the data presented in this Section show that, in the course of the reactions of 1,3,2-diheterophospholans with proton-donating reagents, intermediates with a pentacoordinate phosphorus atom probably play an important role. They can be formed via the 1,1-addition of a nucleophile to the tervalent phosphorus atom, or in a single stage via a three-centre transition stage (A), or in two stages via an ionic intermediate (B)†:



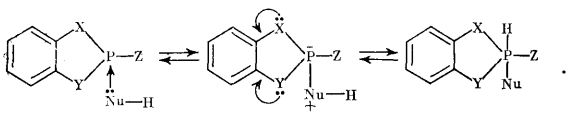
(A)



(B)

†Such reactions are classified in the literature as oxidative addition reactions[72,73].

In those cases where the electrophilicity of phosphorus is fairly high and the negative charge is effectively delocalised in the transition state (or in an anionic intermediate; for example, in benzodiheterophospholans), nucleophilic attack on the tervalent phosphorus atom can precede the proton transfer:

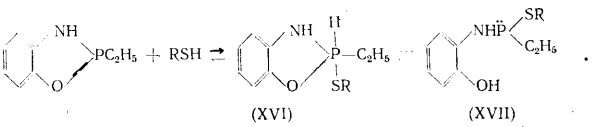


The possibility of the existence of cyclic anions with a tetracoordinate phosphorus atom has been demonstrated in a number of studies[74,75]. There is a possibility of base catalysis in reactions via this pathway[63]. The ability of the phosphorus atom in cyclic compounds to increase fairly readily its coordination number leads in many instances to products with a hexacoordinate phosphorus atom[56–59].

2. Mercaptans and Amines

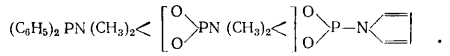
In contrast to alcohols and phenols, mercaptans as a rule convert 1,3,2-diheterophospholans into thiophosphoryl compounds[76,77]. Only in rare instances are exocyclic groups at the tervalent phosphorus atom substituted by an alkylthio-group with retention of the coordination number[63]. The formation of cyclic phosphorothioic acids is observed on interaction of cyclic phosphites with hydrogen sulphide[78–80].

Depending on their structure, 1,3,2-oxazaphospholans react differently with mercaptans. Saturated heterocycles with an alkylene bridge in the molecule undergo "thionation" with retention of the cyclic fragment[63]. On the other hand, 4,5-benzo-1,3,2-oxazophospholans react with mercaptans to form addition products—monocyclic phosphoranes (XVI) with a P–H bond and a small amount of the isomeric phosphonamidothioites (XVII) with a tervalent phosphorus atom[55,81]. Compounds (XVI) and (XVII) are probably involved in a tautomeric equilibrium, which is displaced towards compound (XVI):



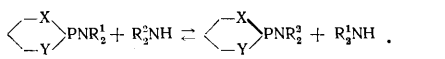
(XVI) (XVII)

The aminolysis of cyclic phosphorus(III) derivatives has been studied in greatest detail in relation to 1,3,2-dioxaphospholans having an exocyclic P–N bond[37]. The reactivity of cyclic phosphoramidites in transamidation is as a rule higher than that of their acyclic analogues and depends on the nature of the attacking and leaving amines. The rate of aminolysis increases with increasing basicity of the amine and the electrophilicity of the phosphorus atom in the sequence[82]



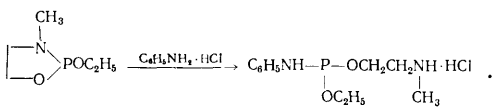
At the same time instances of the substitution of a more basic amine by a less basic amine in the presence of acid admixtures are known. The reactions take place in such cases in the three-component phosphoramidite–acid–amine system via the initial protonation of the phosphoramidite and subsequent formation of an anhydride, which interacts with the less basic amine to form transamidation products[62,83].

On the other hand, in a study of the transamidation of 2-dialkylamino-1,3,2-dioxa- and 1,3-dimethyl-1,3,2-diazaphosphorinanes, it was suggested that the following equilibrium obtains as a rule in the phosphoramidite–amine system[61]:

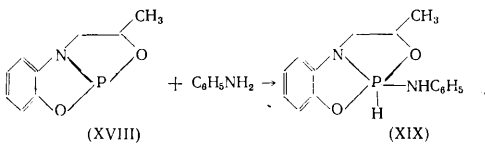


The role of added acid consists in shifting the equilibrium as a result of the binding of the more basic amine. However, this view is apparently valid only when equimolar amounts of the acid are used and does not explain the catalytic influence of the acid reactant on the course of these reactions.

The aminolysis of the endocyclic P–N bond in 1,3,2-oxazaphospholans takes place when aniline hydrochloride is used; in the absence of added additives, these reactions do not occur[84]:

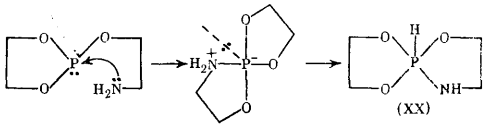


The aminolysis of 1,3,2-diheterophospholans can also proceed via the intermediate formation of phosphoranes with a P–H bond[53]. The present authors have detected addition products of this type by ^{31}P NMR in a study of the interaction of bicyclic phosphoramidites with primary and secondary amines. After mixing the bicyclic compound (XVIII) with aniline at room temperature, a doublet signal was recorded in the ^{31}P NMR spectrum of the reaction mixture ($\delta_{^{31}P}$ = −54 p.p.m., $^1J_{PH}$ = 820 Hz); it refers to the phosphorane (XIX):



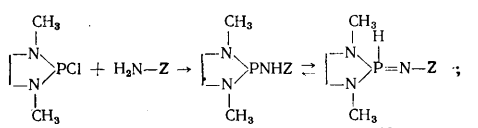
(XVIII) (XIX)

The reaction with diethylamine is accompanied by an exothermic effect and also leads to an addition product with a pentacoordinate phosphorus atom ($\delta_{^{31}P}$ = −42 p.p.m., $^1J_{PH}$ = 820 Hz). The increase of the rate of reaction in the sequence diphenylamine < ethylaniline < diethylamine suggests that in such cases there is nucleophilic attack on the tervalent phosphorus atom, which functions as the electrophilic reactant. An analogous mechanism must be assumed also in cyclisation reactions with formation of spirophosphoranes, for example, compound (XX):[2]



(XX)

Products with an exocyclic secondary amino-group, which in many instances exist in the tautomeric imide form, have been obtained by the amination of 2-halogeno-1,3,2-diazaphospholans[85]:

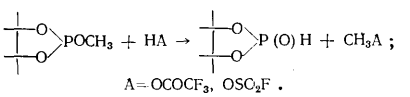


Z=SO_2CF_3, $SO_2C_6H_4$–CH_3, P(S)$(OC_6H_5)_2$, P(S)$(C_6H_5)_2$.

3. Acids

The reactions of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes with strong hydrogen donors, namely carboxylic[48,86–93], sulphonic[53,94,95], and phosphorus-containing acids[96–98], take place in several ways: with ring opening[87,89], with formation of phosphorane and spirophosphorane derivatives[90,91], with formation of disproportionation[48] and polymerisation[92,93] products, and with substitution of an exocyclic group[44,88,89].

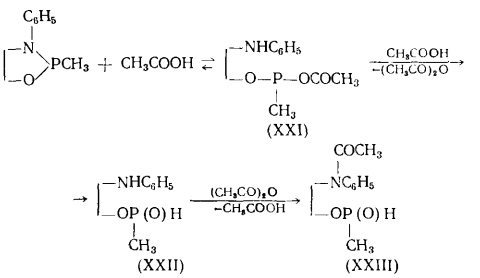
The interaction of the hydrate of toluene-*p*-sulphonic acid with substituted 1,3,2-oxazaphospholans and 1,3,2-oxazaphosphorinanes leads to products of the hydrolytic ring opening[94,95]. When equimolar proportions of the cyclic phosphite and trifluoroacetic or fluorosulphonic acids are used, the ring is not opened; in this case exocyclic dealkylation via the mechanism of the Arbuzov reaction is observed[11]:



A=$OCOCF_3$, OSO_2F .

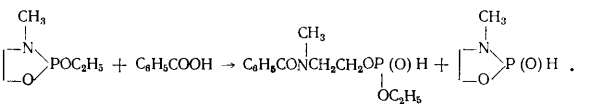
The reactions of strong phosphinic[96] and phosphinodithioic[97] acids with 1,3,2-diheterophosphorinanes resulted in the isolation of mixed anhydrides. The tricoordinate phosphorus atom in the ring of the latter was found to have a reduced nucleophilic reactivity.

The study of the interaction of carboxylic acids with 1,3,2-oxazaphospholans showed that, depending on the structure of the latter, the reactions can involve the nitrogen or phosphorus atom of the P–N ambident system. Protonation of the endocyclic nitrogen atom in saturated 1,3,2-oxazaphospholans leads to ring opening with formation of the phosphonite (XXI). As a result of acidolysis, the latter is converted into the hydrophosphoryl compound (XXII) and the acetic anhydride produced acetylates the amino-group with formation of the compound (XXIII):[89]

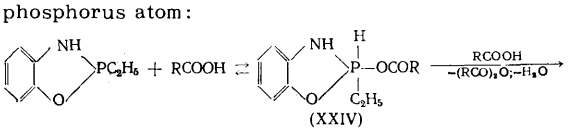


(XXI) (XXII) (XXIII)

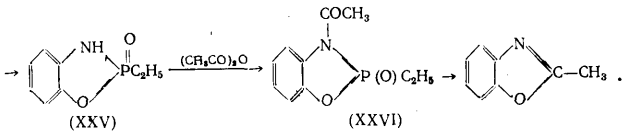
The analogous reaction involving 2-alkoxy-3-alkyl-1,3,2-oxazaphospholans takes place simultaneously via two pathways with formation of linear and cyclic acid phosphites:



2-Ethyl-4,5-benzo-1,3,2-oxazaphospholan reacts with carboxylic acids under mild conditions to form products of the phosphorane type with a P–H bond [compounds (XXIV) [90,91]], which are further converted into compounds (XXV) with a tetracoordinate phosphorus atom. The rate of reaction increases with increase of the strength of the carboxylic acid. The first step in the interaction is probably protonation of the phosphorus atom:



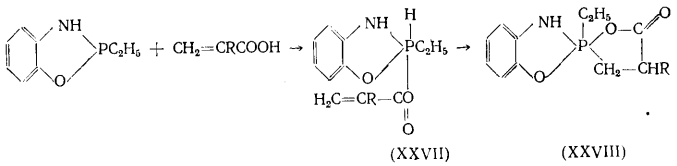
(XXIV)



(XXV) (XXVI)

Acylation of the phosphonate (XXV) by acetic anhydride on heating leads to 2-methylbenzoxazole, formed from the acetylated oxazaphospholan (XXVI).

When α,β-unsaturated carboxylic acids are used, the phosphoranes (XXVII) formed initially are stabilised in a different manner—via intramolecular cyclisation with formation of the spirophosphoranes (XXVIII) with a P–C bond[91]:



(XXVII) (XXVIII)

Analogous reactions of 1,3,2-dioxaphospholans investigated previously lead to the formation of spirophosphoranes and polymeric products[92,93]. The formation of zwitter-ionic intermediates as the result of attack by a phosphonite molecule on the β-carbon atom of the unsaturated acid was postulated for this process[93] (see Section VIII below). However, one cannot rule out the possibility that initial protonation of the phosphorus atom is possible in these reactions too.

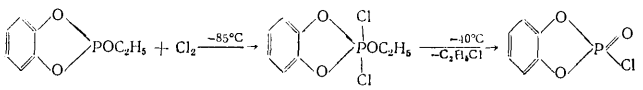
IV. BIPHILIC REACTIONS

Derivatives of tervalent phosphorus can exhibit in many instances a "biphilic" reactivity[99]. "Biphilicity" is understood as the ability of the phosphorus compound not only to supply electrons to the substrate with formation of a σ-bond but also to receive them at the same centre with formation of a σ- or π-bond. Reactions of this type were partly considered in the previous Section devoted to proton-donating reagents. It follows from the foregoing that "biphilic" reactions can be most usefully investigated in relation to cyclic systems in view of the relative stability of the intermediates formed; this makes it possible to investigate the intermediate stages in certain processes.

1. Reactions with Halogens

Depending on their structure, the halogenation of 1,3,2-diheterophospholans can proceed with ring opening and the formation of linear products[100] or it can lead to cyclic phosphates via the mechanism of the Arbuzov reaction[101–103]. In many instances it was possible to note the formation of adducts with a pentacoordinate phosphorus atom[101–106]. The initial formation of phosphonium salts of type (XXIX) has been assumed in these reactions[107]. They can be converted into the final products (XXX) and (XXXI) via two pathways: as a result of the attack by the halide ion on the phosphonium centre (pathway *a*) or as a result of the attack on another electrophilic centre of the molecule—the tervalent phosphorus atom (pathway *b*, Scheme 2):

The chlorination of 2-alkoxy-4,5-benzo-1,3,2-dioxaphospholans in methylene chloride at −85 °C made it possible to detect the formation of the dichlorophosphorane (XXXII) which is converted into the cyclic phosphorochloridate (XXXIII) on raising the temperature to −40 °C:[108–110]



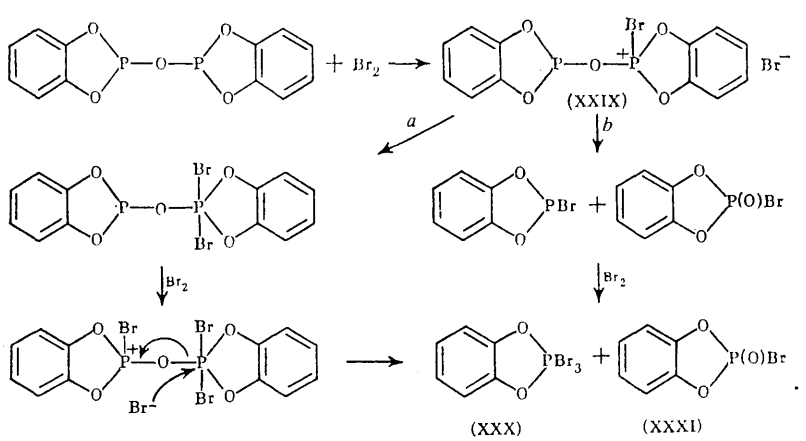
(XXXII) (XXXIII)

The analogous reaction of 4,5-benzo-1,3,2-dioxaphospholan, obtained from the optically active secondary *R*(+)-octyl alcohol, leads to a halogenoalkane with the *S*(−)-configuration[109]. This enabled the authors[109] to suggest that the process illustrated in Scheme 3 proceeds via a stage involving the formation of the dihalogenophosphorane (XXXIV), which is involved in a rapid equilibrium with the phosphonium salt (XXXV).

The dealkylation of the latter via the S_N2 mechanism leads to substitution at the chiral carbon atom with inversion of its configuration. The alternative mechanism with a four-centre transition stage (XXXVI) would lead to the retention of the configuration of the carbon atom in the exocyclic alkoxy-group.

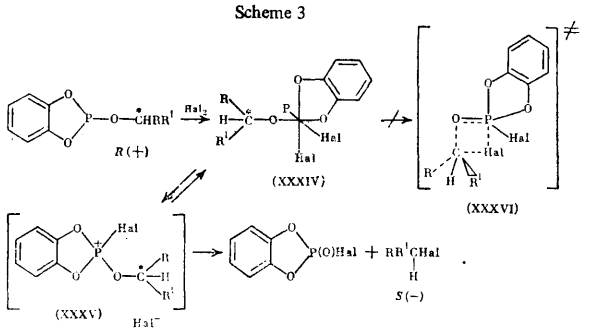
Halogenation of oxazophospholans leads to the opening of the ring at the phosphorus–oxygen bond and the formation of phosphoramidochloridates[111]. The stereochemical result of the halogenation of *cis*- and *trans*-2-methoxy-1,3,2-dioxaphosphorinanes[112] depends on the nature of the halogen: chlorination takes place stereospecifically and bromination yields a mixture of diastereoisomeric products in which one or other diastereoisomer predominates.

Scheme 2



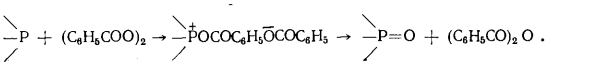
(XXIX) (XXX) (XXXI)

Scheme 3



2. Reactions with Peroxides, Disulphides, and Dithiocyanogen

Cyclic and linear derivatives of tervalent phosphorus are characterised by a high reactivity in reactions with peroxides[113–115]. It has been suggested that the interaction with benzoyl peroxide takes place via the initial attack by the phosphorus atom on the peroxide oxygen with formation of the ion pair (XXXVII):

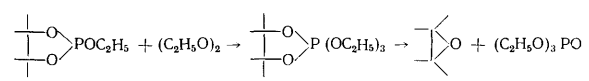


(XXXVII)

The sequence of changes in the reactivity of the cyclic phosphoramidites is analogous to that observed in the reactions with alkyl halides (see Section 5).

The results of a study of the reactions of cyclic phosphites with diethyl peroxide lead to a different conclusion[114]. The rate of this reaction increases in the sequence acyclic phosphites < dioxaphosphorinanes < dioxaphospholans.

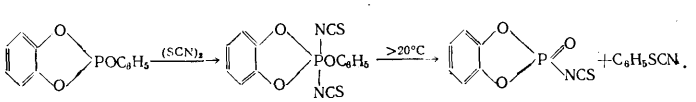
Among the phospholan derivatives, the 4,5-benzo-derivative, in which the phenylenedioxy-substituent exhibits powerful electron accepting properties, shows the highest reactivity. In addition, one should note the instability of the cyclic phosphoranes (XXXVIII) formed in the reaction:



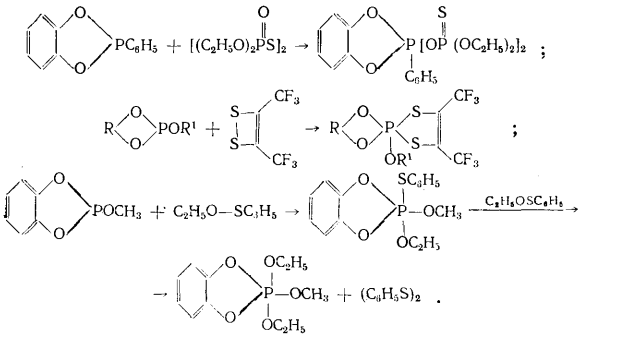
(XXXVIII)

These results are consistent with the concept of the "biphilic" insertion of the phosphorus atom of the cyclic phosphite in the oxygen–oxygen bond of the peroxide. The 1,3,2-diazaphospholan analogues also react with diethyl peroxide to form the corresponding pentacoordinate compounds, but their stability is much lower than that of the intermediates with oxygen-containing rings[116].

A series of reactions accompanied by the "biphilic" insertion of tervalent phosphorus derivatives in the O–S and S–S bonds have been described in the literature. The reaction of 2-phenoxy-4,5-benzo-1,3,2-dioxaphospholan with dithiocyanogen[117] results in the formation of quinquevalent phosphorus compounds containing P–N bonds:



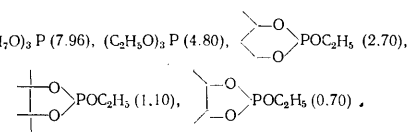
The formation of phosphorane derivatives is observed in the reactions of cyclic phosphites with disulphides[117–119] and compounds containing the O–S bonds[120]:



V. THE ARBUZOV REACTION. REARRANGEMENTS

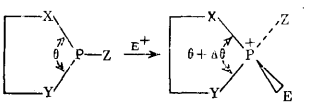
The study of the behaviour of cyclic esters of phosphorus acid in reactions with alkyl halides was initiated by Arbuzov in the 1950's.[121] The structure of the final products of this reaction depends on the ring size and the number and nature of its substituents. According to the results of differential thermal analysis[122], acyclic phosphites enter most readily into the Arbuzov reaction, while their 1,3,2-dioxaphosphorinane and 1,3,2-dioxaphospholan analogues react with greater difficulty. The increase of reactivity corresponds to the increase of electron density at the ring phosphorus atom[2,123].

A study of the comparative reactivities of tervalent phosphorus acid esters with respect to CH_3I established that, on passing from linear trialkyl phosphites to their six- and five-membered cyclic analogues, the rate constant diminishes[124]:



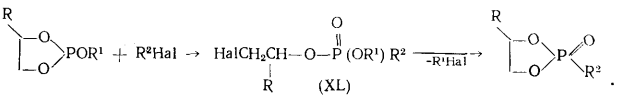
The values of $10^4\ k$ (litre $mol^{-1}\ s^{-1}$) are given in brackets.

The lower reactivity of phospholan derivatives in reactions with electrophiles E^+ is explained from the standpoint of the increasing ring strain ($\theta + \Delta\theta$) in the transition state, because the endocyclic angle increases from 93–98° to 109° in the intermediate (XXXIX) formed with a quaternised phosphorus atom[2,125]:



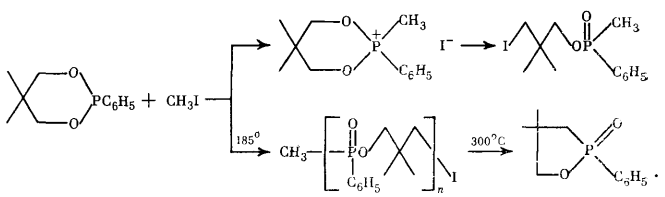
(XXXIX)

The Arbuzov reaction involving the esters of pinacol- and methoxymethylethylene-phosphorous acids as well as esters with six-membered rings proceeds without ring opening[126]. The reaction involving phosphites with cyclic arylene substituents takes place analogously[127,128]. Unsubstituted or monosubstituted phospholan systems tend to undergo ring opening[129–131], but there is also a possibility of the subsequent cyclisation of the intermediate linear phosphonate (XL):[132,133]

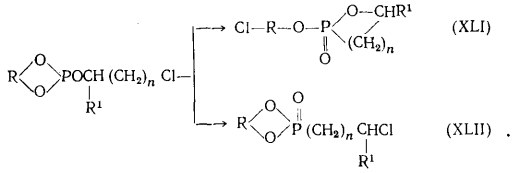


(XL)

In the reaction of methyl iodide with neopentylene phenylphosphonite[134], there is a possibility of "transcyclisation" at a high temperature with formation of an oxaphospholan derivative together with the usual Arbuzov reaction:

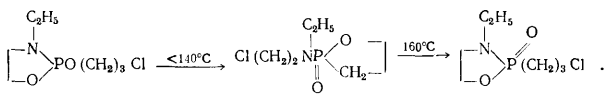


2-(ω-Halogenoalkoxy)-1,3,2-diheterophosphacycloalkanes, formed in the reaction of cyclic phosphorochlorodites with epoxyalkanes, undergo an unusual intramolecular version of the Arbuzov rearrangement[135-144]. The cyclic fragment of the initial phosphite can then be quoted or can be retained depending on the size of the ring, the nature and number of its substituents, and also the structure of the exocyclic halogenoalkyl component[137-145]:



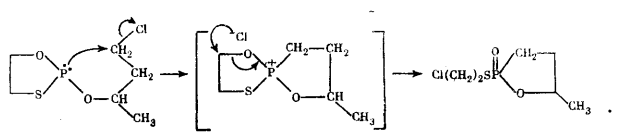
(XLI) (XLII).

In the majority of instances, intramolecular thermal isomerisation leads to a mixture of the isomeric compounds (XLI) and (XLII). The rearrangement of ethylene and 1,2-propylene phosphite results in the formation of both products; on the other hand, 2,3-butylene phosphites isomerise preferentially to compounds (XLII) with retention of the phospholan ring. The ratio of the isomers formed depends also on temperature. Thus 1,3,2-oxazophospholan (XLIII) isomerises at 140 °C to 1,2-oxaphospholan (XLIV) and an increase of the reaction temperature leads to "transcyclisation" with formation of a compound having the oxazaphospholan structure (XLV):[141]



(XLIII) (XLIV) (XLV).

The ease of isomerisation depends on the nature of the branching of the exocyclic fragment. The introduction of the methyl group in the γ-position in the 3-chloroalkoxymoiety can fully suppress the intramolecular isomerisation of oxazaphospholans; the presence of the methyl group in the α-position facilitates the reaction[141]. These data are satisfactorily consistent with the S_N2 mechanism of the substitution of the halogen by a phosphorus atom at the terminal carbon atom. The rearrangement of the oxathiaphospholans (XLVI) is accompanied by ring opening at the C–O bond[140], probably via the attack by the chloride ion on the carbon of the unsubstituted oxathiaphospholan quasi-phosphonium intermediate (XLVII):



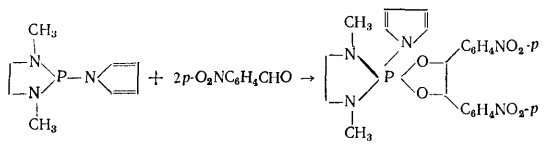
(XLVI) (XLVII).

VI. REACTIONS WITH CARBONYL COMPOUNDS

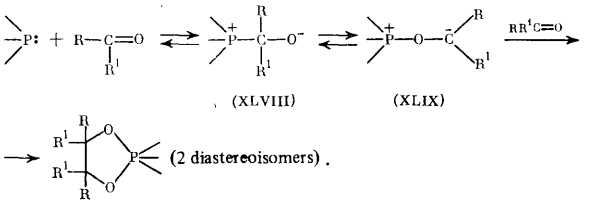
1. Aldehydes and Ketones

Data on the chemical reactions of alkylene phosphites with α-halogenoaldehydes and ketones have been published in a review[10] and will not be considered here. One should only note that α-chloroaldehydes interact with cyclic phosphites to form cyclic and acyclic products of the Perkow reaction, while α-chloroketones react both via the mechanism of the Arbuzov reaction and that of the Perkow reaction.

Various 1,3,2-diheterophospholans interact with aromatic aldehydes and ketones to form 1:2 adducts with the spirophosphorane structure[146-150]:

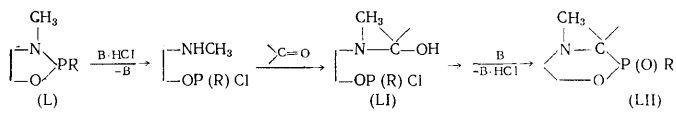


Apparently spiro-cyclisation takes place via the formation of intermediate dipolar structures (XLVIII) and (XLIX), which are converted into compounds with a pentacovalent phosphorus atom on reaction with a second molecule of the carbonyl reagent[1,151]:



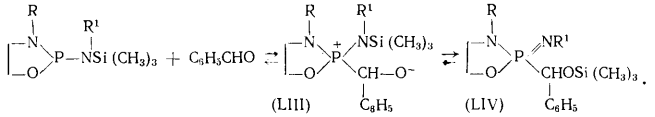
(XLVIII) (XLIX) (2 diastereoisomers).

The interaction of oxazaphospholans with aldehydes and ketones is frequently accompanied by the insertion of the latter in the P–N bond, ring expansion, and the formation of 1,4,2-oxazaphosphorinanes[152-156]. In these reactions there is acid catalysis due to an admixture of the hydrochlorides, frequently present in the initial cyclic phosphoramidites[157,158]. Under their influence, the initial dissociation of the P–N bond of the oxazaphospholan (L) takes place[159] and the resulting aminoalkyl phosphorochloridite or phosphonochloridite interacts with the carbonyl compound; the dehydrochlorination of the intermediate (LI) leads to the corresponding 1,4,2-oxazaphosphorinane (LII):



(L) (LI) (LII).

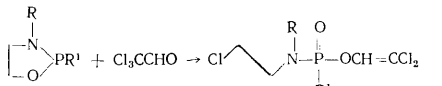
The reactions of carbonyl compounds with 1,3,2-oxazaphospholans containing the silylamino-group in the exocyclic fragment take place readily[160,161]:



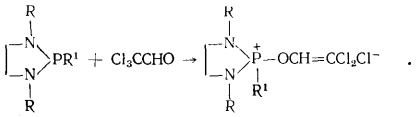
(LIII) (LIV).

The nucleophilic addition of the phosphorus(III) atom of the initial phosphoramidite to the carbonyl group leads to the formation of the dipolar ion (LIII), in which the trimethylsilyl group migrates to the oxy-anionic centre. The cyclic phosphonate (LIV) formed decomposes on heating into the initial component via a stage involving the formation of compound (LIII).[160]

2-Alkoxy-1,3,2-oxaza- and 2-alkoxy-1,3,2-diaza-phospholans react differently with chloral. The formation of products with ring opening, namely β,β-dichlorovinyl phosphates (LV), is characteristic of the former[162], while the latter give rise to cyclic phosphonium chlorides (LVI):[163]



(LV)

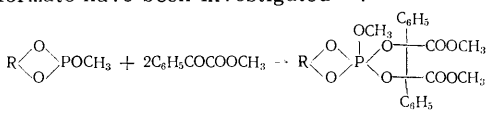


(LVI)

The study of the reactions of substituted 1,3,2-diheterophosphacycloalkanes with chloral and trichloroacetophenone[164] established that the overall sequence of the changes in the reactivity of cyclic phosphites in this process resembles that established in reactions of cyclic phosphites with alkyl halides[165] (see Section V): the reactivity decreases on passing from acyclic derivatives of tervalent phosphorus to their six- and five-membered cyclic analogues. This agrees with the idea that the rate-determining stage in such reactions involves the attack by the phosphorus atom on the carbon atom of the carbonyl group.

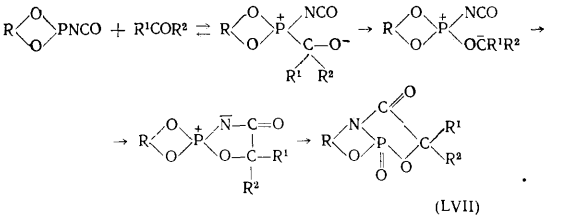
2. Activated Carbonyl and Dicarbonyl Compounds

The reactions of trialkyl phosphites with carbonyl compounds activated by electron-accepting substituents can take place via two pathways[151]: at a low temperature with formation of predominantly pentacoordinate derivatives of phosphorus and at an elevated temperature with formation of the corresponding 2-substituted alkyl phosphonates. In contrast to linear phosphites, the cyclic analogues give rise as a rule to the thermodynamically stable spirophosphoranes. This is observed in the reactions of ethers and amides of alkylene phosphorous acids with esters of α-ketoacids[166] and of 1,3,2-diheterophospholans with phenylbenzoyldiimide[167,168] and the esters and the nitrile of benzoylformic acid[169,170]. The kinetics of the reactions of cyclic phosphites with methyl benzoylformate have been investigated[171]:



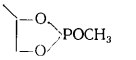
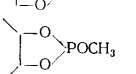
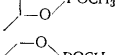
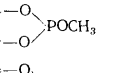
Despite the fact that two ester molecules participate in the reaction, the rate of the process is described by a second order kinetic equation (or first order with respect to each reactant) and the slowest stage is the formation of a dipolar ion of the type $\geq\overset{+}{P}-\underset{|}{C}-O^-$ (XLVIII).[171] The thermodynamic characteristics obtained (Table 1) make it possible to assign the five- and six-membered cyclic analogues to various reaction series: the reactivity of the phospholan derivatives is controlled by the entropy factor, while the reactions of phosphorinane derivatives are subject to control by the enthalpy factor.

The products of the interaction of cyclic phosphoroisocyanatidites with the esters of pyruvic, benzoylformic, and α,β-di-oxobutyric acids and phenylglyoxal[172-174] are the corresponding hetero-derivatives of the bicyclo-octane and bicyclononane series (LVII):



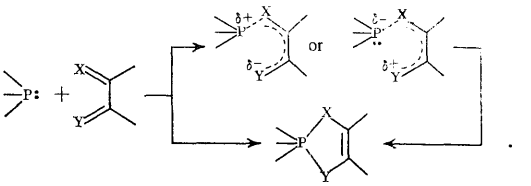
(LVII)

Table 1. Kinetic parameters of the reactions of cyclic phosphites with benzoylformic acid ester at 50 °C.[171]

Phosphite	$10^4 k$, litre mol^{-1} s^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
	5.60	16.4	249.5
	9.10	19.3	236.9
	14.02	26.5	210.8
	1.69	5.9	292.7
	2.65	3.8	295.7

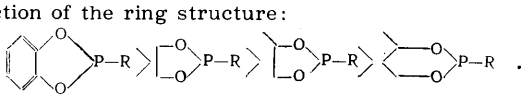
The interaction of cyclic derivatives of tervalent phosphorus with dicarbonyl and saturated carbonyl compounds has been examined in reviews[1,151,175]. 1,3,2-Diheterophospholans react with α,β-unsaturated compounds containing the N=N–C=O and N=C–C=O conjugated systems, which results in the formation of spirophosphorane structures[176-180].

Such processes resemble the cycloaddition reactions, which can proceed either via two stages or synchronously. The characteristics of such reactions are consistent with the mechanism of diene condensation with participation of cyclic phosphites[181-188]:



The rate of reaction depends mainly on the redistribution of electron density in the intermediate reaction complex, which results in the manifestation of the dominant influence of electronic or steric factors (Table 2).

The replacement of acyclic groups by cyclic groups increases significantly the rate and lowers the activation barrier to the reaction owing to the weak electron-donating influence of the 1,3,2-dioxaphospholan fragment compared with the two alkoxy-groups in the transition state. The activity series of cyclic phosphites in diene condensation[181,182] has been established as a function of the ring structure:



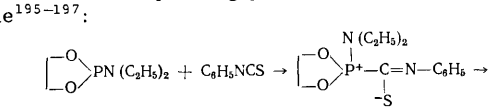
The data obtained most probably indicate nucleophilic attack by the unsaturated reactant; phosphorus then exhibits electrophilic properties[189]. The successive replacement of the oxygen atoms in the diheterophospholan fragment by sulphur apparently increases still further the electron-accepting character of this fragment and increases the rate of condensation[183].

Table 2. Kinetic parameters of the condensation reactions between phosphorochloridites and isoprene[184].

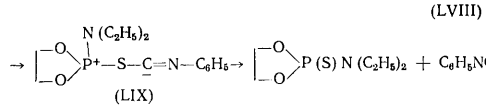
Phosphorochloridite	$10^4 \cdot k$, litre mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
$(C_2H_5O)_2PCl$	0.012	92.8	100.8
	0.97	70.1	150.8
$C_2H_5OPCl_2$	1.26	82.3	116.8

3. Reactions with Isocyanates, Carbon Dioxide, Their Thio-analogues, and Related Compounds

The "insertion reactions" involving isocyanates, isothiocyanates, carbon disulphide, carbon dioxide, and other heterocumulated reagents occupy a special place in the chemistry of tervalent phosphorus acid amides[190,191]. It has been suggested[192] that the reaction takes place via the insertion of the carbonyl reactant in the P–N bond in the ring with formation of an intermediate with a larger cyclic system than in the initial phosphite. However, it was shown subsequently[193,194] that two independent pathways can be followed in these reactions: insertion in the ring of the diheterophosphacycloalkane and its oxidation with formation of a compound having a tetrahedral phosphorus atom. In the interaction of cyclic phosphoramidites with isothiocyanates, dipolar ions with a P–C bond (LVIII) arise in the first stage and readily undergo the mercaptophosphonate–phosphorothioate rearrangement in the course of the reaction to the thiophosphonium intermediate (LIX); the final reaction products are the corresponding phosphoramidothioate and an isonitrile[195–197]:



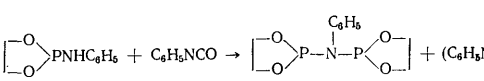
(LVIII)



(LIX)

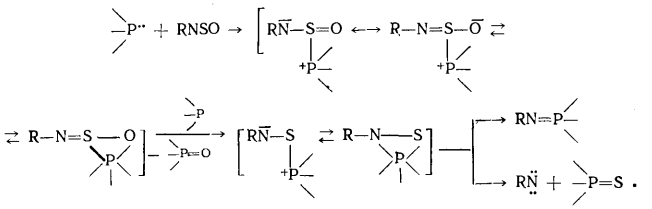
Cyclic phosphoramidites are oxidised analogously by isocyanates.

The presence of a mobile hydrogen atom in the exocyclic amino-group of the 1,3,2-dioxaphospholan permits its disproportionation in the reaction with isocyanate[197,198]:

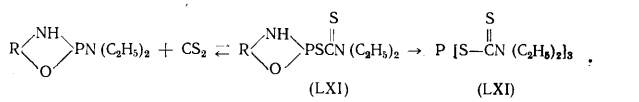


As a consequence of their low nucleophilic reactivity, 1,3,2-diheterophospholans are less reactive in reactions with substituted sulphenylamines than their open-chain analogues[199].

It has been suggested that the process begins with nucleophilic attack by the phosphorus atom on the electrophilic sulphur atom; in the subsequent stages the S–O and P–S bonds in the intermediates formed dissociate simultaneously or in succession. The final products of the reaction are the corresponding phosphoryl, thiophosphoryl, and imidophosphoryl derivatives:



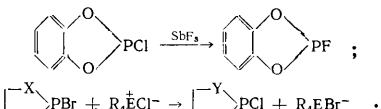
The stability of the products of the insertion of CS_2 and CO_2 in the exocyclic P–N bonds of 1,3,2-dioxaphosphorinanes[200], 1,3,2-oxathiaphospholans, 1,3,2-dithiaphospholans[201], and 1,3,2-oxazaphospholans[202] depends on the structure of the cyclic fragment. As a result of the interaction of carbon disulphide with amides containing a diheteroalkylene cyclic fragment (R = alkylene), stable thiocarbamoyl phosphorothioites (LX) are formed; the reaction of 4,5-benzo-1,3,2-oxazaphospholan (R = *o*-C_6H_4) takes place with subsequent disproportionation of the 1:1 adducts to tris(*N*,*N*-diethylthiocarbamoylthio)phosphine (LXI):



(LXI) (LXI)

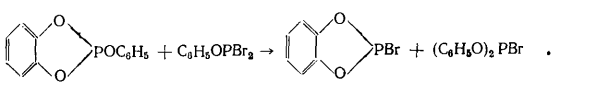
VII. SUBSTITUTION AT THE PHOSPHORUS ATOM ON TREATMENT WITH REAGENTS WITHOUT A MOBILE HYDROGEN ATOM

As already mentioned above, reactions accompanied by the substitution of the exocyclic group at the phosphorus atom are extremely characteristic of cyclic phosphorus derivatives. This is also characteristic of a series of reactions involving reagents without a proton. It has been established[203] that there is rapid intermolecular halogen exchange involving 2-chloro(bromo)-1,3,2-dioxa(oxaza)phospholans. The activation barrier to this process is 20.2 ± 4 kJ mol^{-1}, which agrees with the idea that the mechanism of the exchange involves a four-centre transition state of type (XV) without the preliminary ionisation of the phosphorus–halogen bonds. The exocyclic chlorine is readily substituted by fluorine on treatment with antimony trifluoride and bromine is substituted by chlorine on treatment with ammonium, phosphonium, and arsonium chlorides[204–206]:

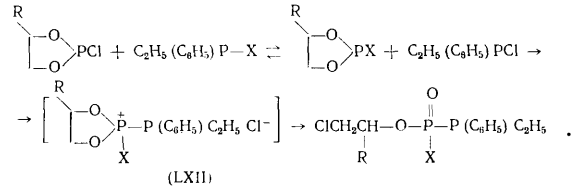


X, Y=O, NR; R=Alk, Ar; E=N, P, As .

The exchange of substituents has been noted in reactions of the full cyclic esters of phosphorous acid[207,208]:

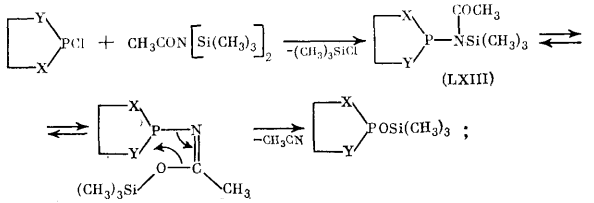


Similar exchange processes have been demonstrated also for cyclic phosphorochloridites when these react with trialkyl phosphites or phosphoramidites[209]. In a few instances these processes are accompanied by ring opening via a mechanism of the type of the Arbuzov rearrangement via an intermediate—the cyclic quasi-phosphonium salt (LXII):[210]



(LXII)

2-Halogeno-1,3,2-diheterophospholans are readily silylated by *N*,*N*-bis(trimethylsilyl)acetamide[211–214]:



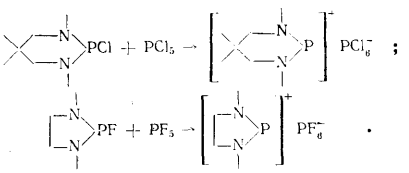
(LXIII)

X, Y = O, NCH_3, NC_6H_5 .

During the reaction, the 2-(*N*-acetyl-*N*-trimethylsilylamino)-1,3,2-diheterophospholans (LXIII) formed initially decompose to the corresponding cyclic silyl phosphites. According to the results of differential thermal analysis, the reactivity of cyclic phosphorohalidites increases on passing from 1,3,2-diazaphospholan to the oxaza- and dioxa-derivatives, i.e. with increasing electrophilicity of the phosphorus atom[211].

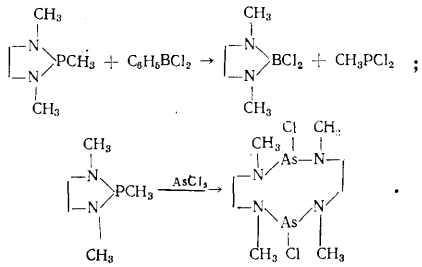
Compounds with a P–P bond can be obtained by treating 2-halogeno-1,3,2-diheterophosphacycloalkanes with metallic sodium[215,216].

Treatment of phosphorohalidites with Lewis acids leads to cyclic cations with a dicoordinate phosphorus atom[19,217]:

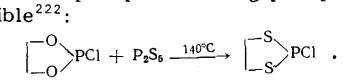


The formation of such compounds has been noted also in the formation of complexes by iron and manganese carbonyls or of fluoroboranes with 1,3,2-diazaphospholans[218–220].

The exchange of phosphorus for other heteroatoms is sometimes observed[205,221]:

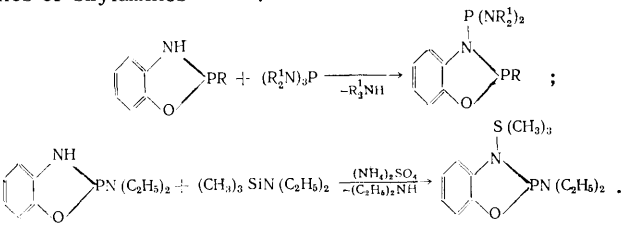


The replacement of the endocyclic oxygen atoms by sulphur in 2-chloro-1,3,2-dioxaphospholan using phosphorus pentasulphide is possible[222]:

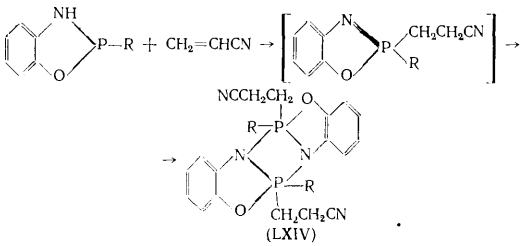


The mechanisms of such reactions have not been determined in detail.

Substitution can take place not only at the phosphorus atom but also at the endocyclic nitrogen atom. 4,5-Benzo-1,3,2-oxazaphospholans readily exchange the mobile hydrogen atoms of the endocyclic amino-group in reactions with triaminophosphines or silylamines[223–229]:



2-Substituted 4,5-benzo-1,3,2-oxaza- and 4,5-benzo-1,3,2-diaza-phospholans readily add to unsaturated compounds with an activated double bond. The addition products formed initially are stabilised via dimerisation to diazadiphosphetidines (LXIV):[229–231]

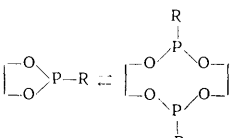


(LXIV)

VIII. RING EXPANSION. POLYMERISATION

In a number of instances cyclic derivatives of tricoordinate phosphorus are capable of spontaneous transformation into dimeric products or oligomers[232]. Thus on standing for a long time, 2-chloro-4,5-benzo-1,3,2-dioxaphospholan is irreversibly converted into oligomeric products, which regenerate the monomeric compound on distillation[233]. A similar reversible transformation of the monomeric 3-methyl-2-phenyl-1,3,2-oxazaphospholan has been noted[193].

The formation of dimers, trimers, and oligomers is particularly characteristic of unsubstituted cyclic derivatives of tervalent phosphorus in which the phosphorus atom is involved in an exocyclic P–C bond. Dioxaphospholans dimerise reversibly to ten-membered cyclic diphosphonites (LXV) in the presence of atmospheric moisture; furthermore, the formation of polymeric compounds is also observed under these conditions[233–237]:



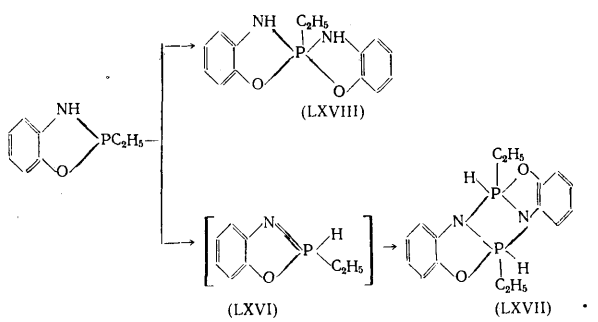
(LXV)

Dimeric derivatives with a similar structure are also formed from 1,3,2-oxazaphospholans[232]. Dimers of type (LXV) retain the properties of tricoordinate phosphorus derivatives —they are oxidised and combine with sulphur[238]. When both endocyclic oxygen atoms are replaced by nitrogen, phospholans lose their tendency to dimerise; ring expansion has not been observed also in the series of 1,3,2-dithiophospholans[236].

After prolonged storage, dioxaphosphorinanes give rise to cyclic dimers and trimers together with polymeric products[239]; in contrast to their five-membered cyclic analogues,

dithiaphosphorinane derivatives with tervalent phosphorus are irreversibly converted into 12-membered cyclic compounds[236].

The dimerisation of 2-ethyl-4,5-benzo-1,3,2-oxazaphospholan takes place in an unusual manner[240]. The phosphonoimidite (LXVI), formed as a result of prototropic isomerisation, dimerises to the diazadiphosphetidine (LXVII); the process is also accompanied by the symmetrisation of the initial phosphonite to give the spirophosphorane (LXVIII):

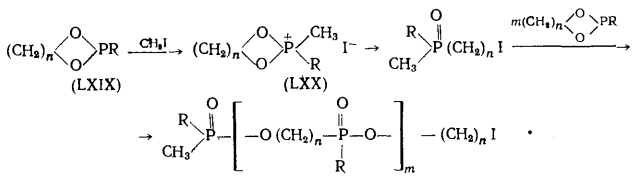


(LXVIII)

(LXVI) (LXVII)

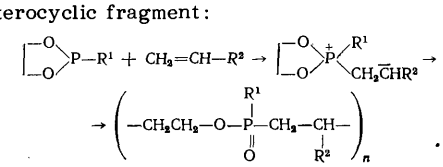
When a ring oxygen atom is replaced by sulphur, the tautomeric prototropic transition does not take place and the formation of the phosphetidine ring is not observed; there is only a reversible transition to a compound having the spirophosphorane structure of type (LXVIII).[241]

The polymerisation and copolymerisation reactions of cyclic derivatives of phosphorus can be initiated by boron trifluoride, sulphuric acid, dimethyl sulphate, and bromocyanoacetamide[242]. The Arbuzov reaction of cyclic phosphites and phosphonites (LXIX) [244] with alkyl halides is used to synthesise oligomers with the phosphorus atom in the main chain; the reaction proceeds via the formation of the quasi-phosphonium salt (LXX), the opening of its ring, and interaction with the next molecule of the phosphacycloalkane:



(LXIX) (LXX)

The polycondensation of the dialkyl esters of phenyl- and ethyl-phosphinous acids with glycols takes place mainly via the intermediate formation of cyclic esters of phosphinous acid[245]. The copolymerisation of cyclic phosphorus(III) derivatives with a wide variety of electrophilic monomers, the so-called alternant polymerisation[93], begins with the formation of the dipolar ion (LXXI): the growth of the polymer chain involves the opening of the ring in the five-membered heterocyclic fragment:



α,β-Unsaturated carboxylic acids, their amides, and sulphonamides as well as ketones have been used as the unsaturated monomers[93].

The data presented in this review demonstrate the unusual reactivity of 1,3,2-diheterophospholans. The characteristics of the geometry of these molecules associated with the incorporation of a tervalent phosphorus atom in a strained five-membered ring alter the character of the hybridisation of the unshared electron pair of the phosphorus atom and weaken the nucleophilic properties of the phosphorus atom compared with acyclic phosphorus(III) derivatives. The distinct tendency of 1,3,2-diheterophospholans to participate in "biphilic" processes with increase of the coordinate number of the phosphorus atom is due to the same causes.

The wide variety of the chemical reactions characteristic of organic phosphorus(III) compounds is supplemented in the case of the cyclic esters, ester-amides, and amides by reactions with ring expansion, "transcyclisation", and spirocyclisation. The comparative instability of the unsubstituted five-membered phosphacycloalkanes containing a phosphorus(III) atom ensures the occurrence of oligomerisation processes, which make these cyclic organophosphorus substances similar to bifunctional monomers.

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Advances in the Chemistry of Amidines

V.G.Granik

The review surveys data published during the period 1971-1981 on the synthesis and physicochemical and chemical properties of various types of amidine systems. Particular attention has been devoted to the use of amidines in the synthesis of heterocycles.
The bibliography includes 259 references.

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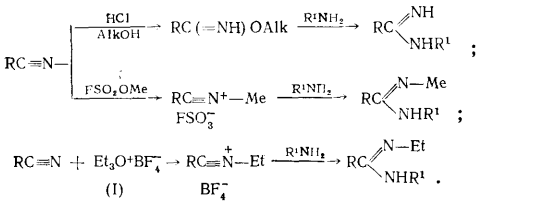
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I. INTRODUCTION

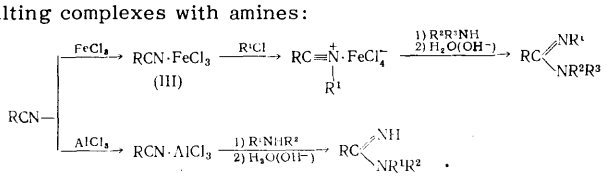
The chemistry of amidines has been recently attracting much attention by investigators in connection with their wide-scale employment in organic synthesis. The number of publications dealing with studies of the methods of synthesis and the properties of amidines has continuously increased and, despite the monograph published in 1975 [1] and a series of reviews dealing with various aspects of the chemistry of these compounds[2-7], most of the data published during the last decade have not been described in the review literature. The present review surveys new data on the synthesis, properties, and reactions of amidine systems of various types, particular attention being devoted to the application of amidines to the synthesis of heterocyclic compounds.

II. METHODS OF SYNTHESIS

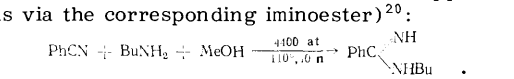
During the period considered, an extremely large number of studies dealing with the synthesis of various amidines were published. The traditional starting materials are nitriles, which are transformed into amidines via intermediate iminoesters. The latter are usually obtained by treatment with hydrogen chloride in alcohol and are then made to react with various amines[8-11]. Another method is based on the alkylation of nitriles with triethyloxonium tetrafluoroborate (I) followed by treatment of the nitrilium tetrafluoroborate salts (II) with amines[12,13]. A modification of this method involves the synthesis of nitrilium salts with the aid of methyl fluorosulphonate[14]:



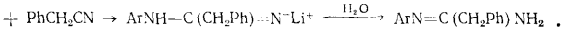
A general method of synthesis of various amidines is based on the reactions of nitriles with Lewis acids ($FeCl_3$ or $AlCl_3$ are usually employed)[15-19] followed by treatment of the resulting complexes with amines:



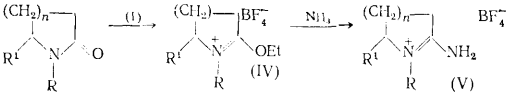
As can be seen from the scheme presented, the complexes of nitriles with iron(III) chloride can be alkylated by alkyl halides to form the corresponding *N*-substituted nitrilium salts, which can be transformed further into *N,N,N'*-trisubstituted amidines. An unusual method of synthesis of amidines at a high pressure is based on the reaction of nitriles with alcohols and amines (the reaction apparently proceeds via the corresponding iminoester)[20]:



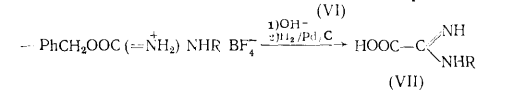
Nitriles can also interact with lithio-derivatives of arylamines[21]:



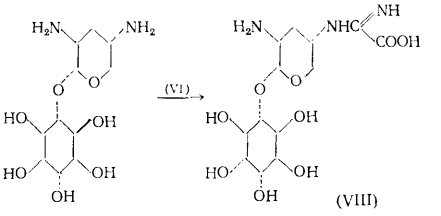
The synthesis of amidines from amides and thioamides is based on the preliminary activation of the amide functional group. Numerous reviews[22-27] dealing with such activation describe, in particular, also a considerable number of amidine syntheses. Such activation is usually achieved by alkylating amides with triethyloxonium tetrafluoroborate (or dimethyl sulphate)[12,28-30] or by acylation with reagents such as hexamethylphosphoramide (HMP),[31,32], phosphoryl chloride[33-35], phosphorus pentoxide[36], and acyl chlorides[37]. Thus the interaction of lactams with compound (I) [28] leads to the formation of the tetrafluoroborates (IV), which then readily react with ammonia to form amidinium salts (V). It is of interest to note that alkylation of 2-pyrrolidinone having a carbamoyl group in the 5-position [compound (IV, R = Me, $R^1 = CONH_2$, $n = 1$)] takes place selectively at the lactam carbonyl[28]:



The reaction involving compound (I) yielded the thioiminoester salt (VI)—the key compound in the method of synthesis of amidinoacids (VII):[29]

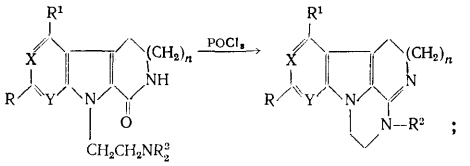


This method has been used in the synthesis of the antibiotic kasugamycin (VIII):[29]



It is of interest that only the equatorial amino-group reacts selectively with compound (VI).[29]

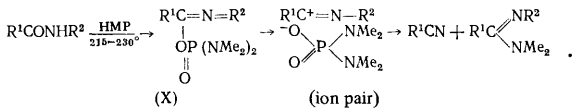
The activation of the amide functional group in tricyclic lactams of type (IX) made it possible to achieve their cyclisation to tetracyclic indole systems containing the amidine fragment[33,35]:



(IX)

X=Y=CH, R^1=R=H, X=Y=N, R^1=R=OH .

When amides are heated with HMP, nitriles and amidines are formed via the phosphorodiamidate derivative (X):[31]



(X) (ion pair)

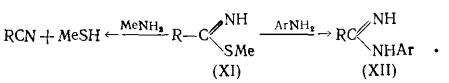
The reaction of an aromatic amine, formic acid, and HMP gives rise to amidines[32]:

$$ArNH_2 + HCOOH \xrightarrow{HMP} ArN{=}CH{-}NMe_2 .$$

The interaction of acetanilides with dimethylformamide (DMF) in the presence of $POCl_3$, $SOCl_2$, PCl_3,[34] P_2O_5,[26] or *N,N*-diethylthiocarbamoyl chloride[37] leads to the corresponding amidines:

$$ArNHCOCH_3 + Me_2NCHO \xrightarrow{POCl_3\ (or\ PCl_3, SOCl_2, P_2O_5, Et_2NCSCl)} ArN{=}CH{-}NMe_2 .$$

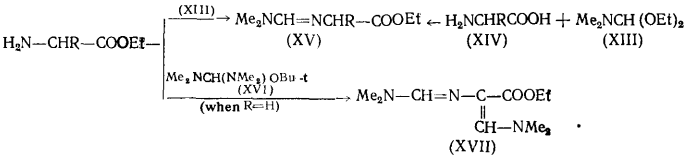
When thioiminoesters (XI) were used in the amidine synthesis, it was established that the esters react with aromatic amines to form the amidines (XII), while the reaction with highly basic amines proceeds with formation of nitriles[38]:



(XI) (XII)

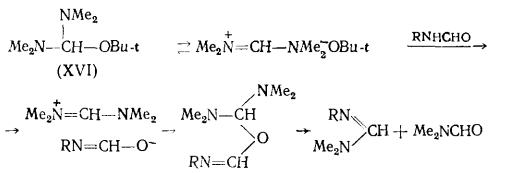
Schnur[38] was able to find a method of synthesis of amidines from compounds (XI) even with the aid of aliphatic amines, which makes it necessary to carry out the reaction in an acetate buffer solution.

Other types of activated amides—amide acetals, lactams, and related compounds, dichloromethyleneimmonium salts, and diethoxymethylammonium salts—are also widely used for the synthesis of amidines. The majority of studies of the amidine synthesis based on these compounds have been described in detail in reviews[25-27,39,40] and here we shall consider only those studies which were not included in the above reviews. A number of investigations were devoted to the synthesis of *N*-heteroarylamidines by the reaction of the acetals of DMF (XIII) and dimethylacetamide with heteroaromatice amines. Derivatives of *N*-pyrazinyl-2-formamidines[41], *N*-pyrimidinyl-2-formamidines[42], *N*-pyridyl-2-formamidines[42], *N*-purinyl-6-formamidines[43], *N*-pyrazolyl-3-formamidines[44], and *N*-pyrazolyl-3-acetamidines[44] were obtained via this procedure. The reaction of compound (XII) with aminoacids (XIV) is accompanied by alkylation and results in the formation of the amidinoesters (XV).[45] Compounds of the same type have also been obtained by the reaction of compound (XIII) with aminoacid esters[46]. When the more reactive aminal-ester (XVI) is used in this reaction, the enaminoamidines (XVII) are formed[46]:

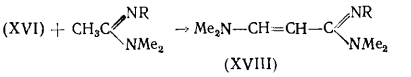


(XV) (XIV) (XIII) (XVI) (XVII)

The reaction of the aminal-ester (XVI) with secondary amides is of interest: *N,N*-disubstituted amides and amidines are formed in this instance. The authors suggested the following reaction mechanism[46]:

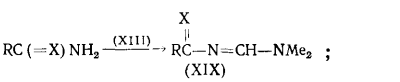


In the same study it was shown that the interaction of the aminal-ester (XVI) with acetamidine derivatives leads to the enaminoamidines (XVIII):[46]



(XVIII)

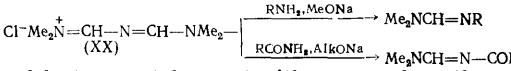
A series of studies have been published recently, according to which the acetal (XIII) readily reacts with primary amides and thioamides, which leads to the formation of acyl- or thioacyl-amidines (XIX)—interesting intermediates in various types of syntheses[47-49]:



(XIX)

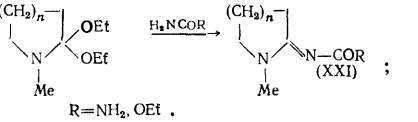
X = O, S .

It has been shown[50] that the immonium salt (XX), obtained previously[51] by the reaction of DMF and cyanuric acid chloride, can be used successfully in the synthesis of amidines and acylamidines instead of the DMF acetal (XIII):



(XX)

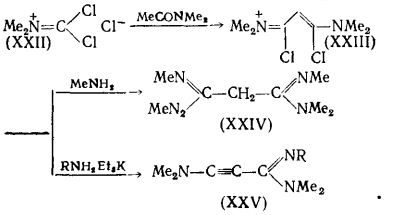
Amide and lactam acetals react with urea and urethane to form the corresponding *N*-carbamoyl- and *N*-ethoxycarbonylamidines (XXI).[52] We may note that the former form complexes with one or several urea molecules:



(XXI)

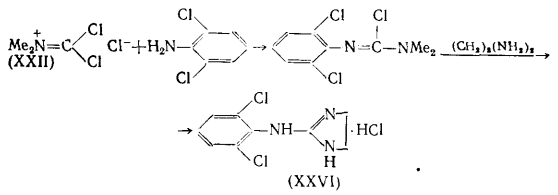
R=NH_2, OEt .

The interaction of dichloromethyleneimmonium chloride (XXII) with *N,N*-dimethylacetamide leads to the salt (XXIII) which can be converted into the diamidines (XXIV) or the ynaminoamidines (XXV), depending on the reaction conditions[53]:



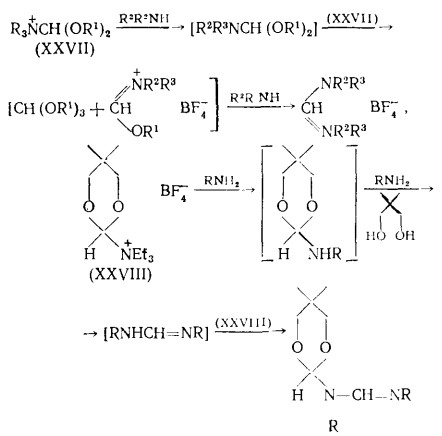
(XXII) (XXIII) (XXIV) (XXV)

A new synthesis of the valuable medicinal preparation clofelin (XXVI), based on the reaction of the immonium chloride (XXII) with 2,6-dichloroaniline involving the intermediate formation of chloroformamidine, was published recently[54]:

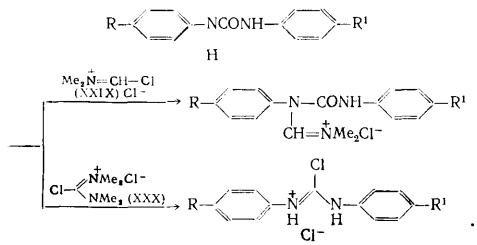


(XXVI)

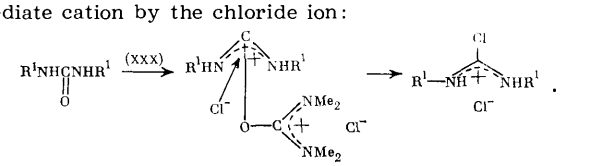
Certain chloroformamidines have been synthesised analogously from compound (XXIII) and different amines including heterocyclic amines[55,56]. A series of substituted formamidines have been synthesised by the reaction of the dialkoxymethylammonium salts (XXVII) and (XXVIII) with aliphatic amines[57,58]:



Processes involving the synthesis of formamidine derivatives by the reaction of diarylureas with chloromethylenedimethylammonium chloride (XXIX) and chlorodimethylaminomethylenedimethylammonium chloride (XXX) are closely related to the reactions described above[59]:

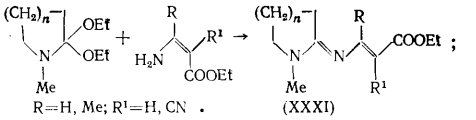


Tritschler and Kausz[57] believe that direct *N*-dimethylaminomethylenation takes place in the former case, while in the latter case it is impossible due to steric hindrance and the reaction involves oxygen with subsequent attack on the intermediate cation by the chloride ion:

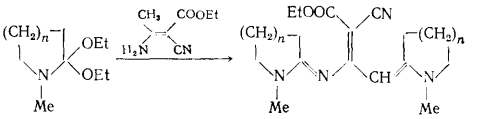


A number of pieces of experimental evidence supporting the above theoretical considerations have been published[59].

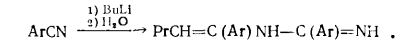
Amide and lactam acetals have also been used in the synthesis of an interesting class of organic compounds—enamidines, which have been used in a number of instances for the synthesis of condensed heterocycles (see below). The enamidines (XXXI) are formed readily and in high yields by the reaction of amide and lactam acetals with primary enamines[60,61], even weakly basic enamines such as aminomethylenecyanoacetic ester:



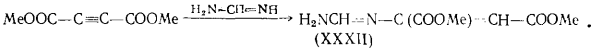
It is of interest to note that the reaction of amide and lactam acetals with β-amino-α-cyanocrotonic ester involves not only the amino-group but also the β-methyl group[61]:



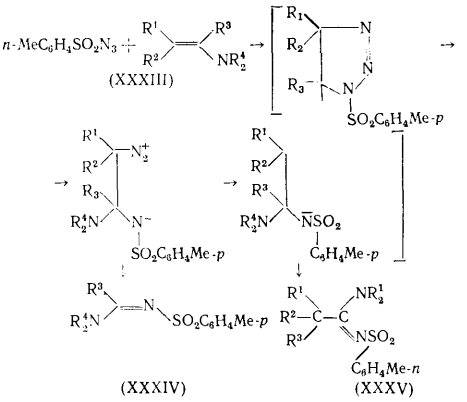
Enamidines have also been synthesised[60,61] by the reaction of aryl cyanides with butyl-lithium or organomagnesium compounds[62,63]:



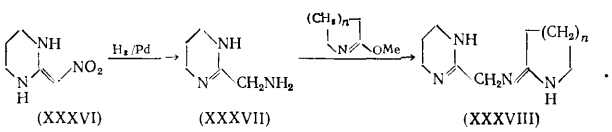
Substituted *sym*-triazines are formed as side products in this reaction[63]. Yet another mention of the synthesis of the enamidine (XXXII) has been made in a study[64] where it was obtained by the reaction of dimethyl acetylenedicarboxylate with formamidine at −10 °C:



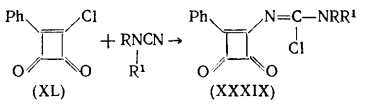
The reaction of the enamines (XXXIII) with toluene-*p*-sulphonyl azide proceeds in a very interesting manner—a mixture of the amidines (XXXIV) and (XXXV) is then formed[65]. It has been noted that, when R^1 and R^2 are alkyls (and not hydrogen atoms), the number of rearranged amidines (XXXV) increases, probably as a consequence of the ability of the alkyl group to stabilise the carbocationic centre:



Amidines (including cyclic amidines) can be obtained by the hydrogenation of nitroalkylenediamines (XXXVI). The bisamidines (XXVIII) have been synthesised from the aminomethylamidines (XXXVII) formed[66]:

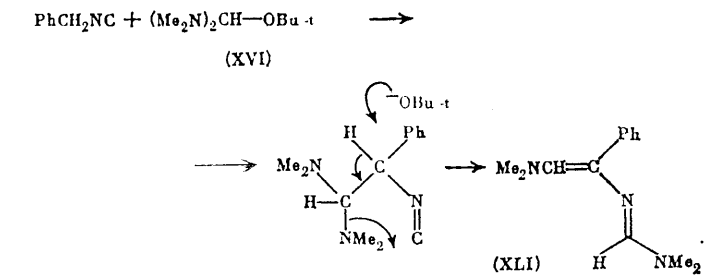


The reduction of carbodiimides with sodium tetrahydroborate[67] or of urea derivatives with lithium tetrahydroaluminate[68] leads to formamidine derivatives. Various formamidines can be synthesised from urea and thiourea derivatives. Thus chloroformamidines are formed when *N*,*N'*-dialkyl-*N*-heteroarylureas react with Ph_3P and CCl_4 [69] or on chlorination of *N*,*N'*-bis(arenesulphonyl)-*S*-methylisothioureas[70]. The chloroformamidine (XXXIX) is also formed on reaction of halogenocyclobutenedione (XL) with cyanamides[71]:



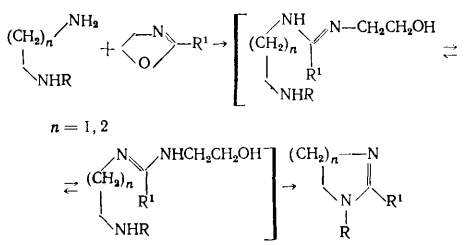
(XL) (XXXIX)

N-Hydroxyamidines have been obtained by the reaction of chloroimides with hydroxylamine[72,73] or by the reaction of substituted hydroximoyl chlorides with amines[74]. The reactions of isonitriles with sulphonamides[75], amines[76–78], and an aminal-ester[46] are used very frequently for the synthesis of amidines. One should note that it has been shown[76,77] that the reactions involving the addition of secondary amines to isonitriles take place stereospecifically with formation of *Z*-formamidines, which then rearrange to the thermodynamically more stable *E*-isomers. The interaction of the aminal-ester (XVI) with benzyl isocyanide involves the methylene unit with subsequent rearrangement[46] involving the formation of the amidine (XLI):

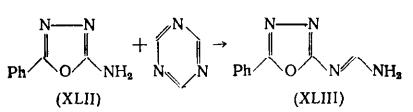


(XVI) (XLI)

A number of studies have been devoted to the synthesis of amidines using certain heterocyclic agents in the corresponding reactions. Thus the reaction of derivatives of ethylene- and propylene-diamines with Δ^2-1,3-oxazoline leads to cyclic amidines[79]:

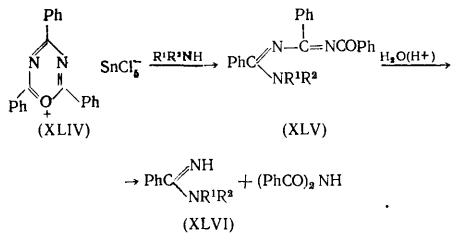


The reaction of 2-amino-5-phenyl-1,3,4-oxadiazole (XLII) with *sym*-triazine leads to the formamidine derivative (XLIII):[80]



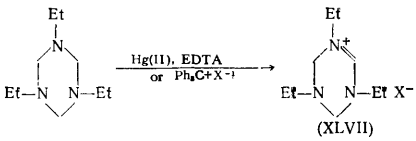
(XLII) (XLIII)

When 1,3,5-oxadiazinium salts (XLIV) react with amines, the products are *N*-(*N*-benzoylimino)benzylamidines (XLV), which hydrolyse in an acid medium to benzamidines (XLVI) and dibenzoylamine[81]:



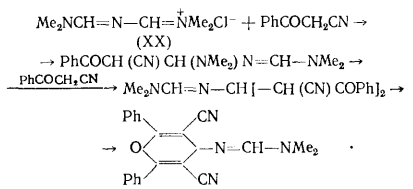
(XLIV) (XLV) (XLVI)

Cyclic amidinium salts (XLVII) can be obtained by oxidising *N*,*N'*,*N''*-triethylhexahydrotriazine or by treating it with $Ph_3C^+X^-$:[82]

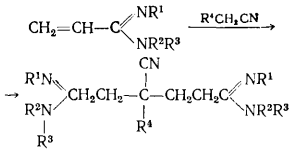


(XLVII)

It has been shown recently[83] that the immonium salt (XX) can be used to introduce the formamidine fragment into compounds with an active methylene unit:



It has been established in recent years that the amidinium group can be introduced into various organic compounds (amines, alcohols, compounds with an active methylene unit, and mercaptans) by the amidinoethylation reaction which is of the same type as the Michael reaction[84–87], for example:

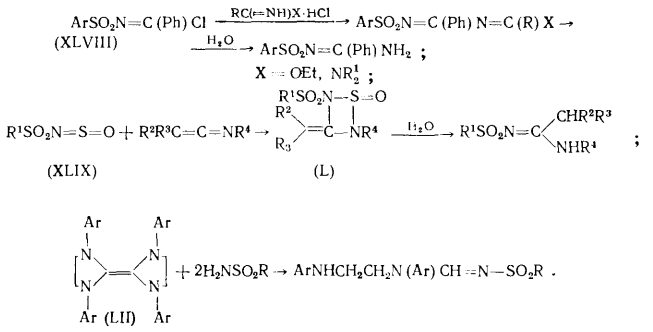


Derivatives of formamidine and homologous amidines are formed when alkali metal amides react with aldehydes in liquid ammonia[88] and *N*,*N'*-dimethylformamidine has been obtained by the thermal decomposition of potassium methylamide[89].

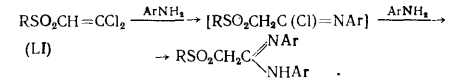
A series of studies have been devoted to the synthesis of amidines with sulphur-, phosphorus-, and silicon-containing substituents at the nitrogen atoms†. Thus sulphonylamidines have been synthesised by the reaction of arenesulphonylchloroimides (XLVIII) with iminoester (or amidine) hydrochlorides followed by the hydrolysis of the intermediate or imidoylamidines[90], by the reaction of *N*-sulphinylsulphonamides (XLIX) with keten imines via [2 + 2] cycloadditions

†See also the study[65] described earlier in this review, which was transferred to the section dealing with the synthesis of amidines from enamine compounds.

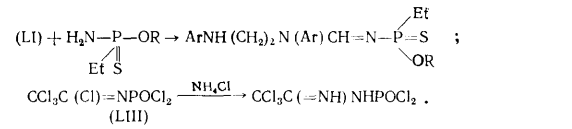
(L),[91] and by the reactions of sulphonamides with the ethylenetetramine (LI):[92]



The reaction of dichlorovinyl sulphones (LII) with aromatic amines takes place via the intermediate formation of chloroimides[93]:

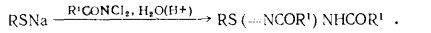


Phosphorus-containing amidines have been synthesised by the phosphorylation of the ethylenetetramine (LI) [92] and also by the reaction of the chloroimide (LIII) or related compounds with ammonium salts[94]:

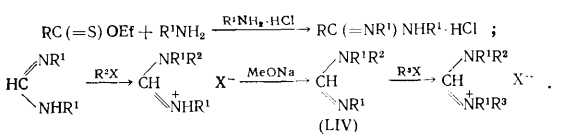


In addition, compounds of this type can be synthesised by the reaction of *N*-unsubstituted amidines with phosphorus halides[95,96]. *N*-Trimethylsilylamidines have been obtained analogously by the reaction of amidines with chlorotrimethylsilane; they are also formed in the reaction of trimethylsilylamine with butyl-lithium, followed by the treatment of the lithio-derivative with chloroimides[97].

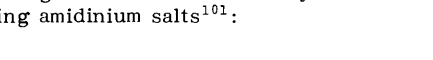
Sulphinamidines, which are an interesting class of compounds, have been synthesised by the reactions of *N*,*N*-dichlorourea[98], *N*,*N*-dichloroamines[99], or *N*,*N*-dichloroamides of diphenoxyphosphoric acid[100] with sodium thiolates:



In conclusion of this section, we may point out two new syntheses of amidines, the first of which is based on the reaction of *O*-ethyl thioesters with amines in the presence of their hydrochlorides[101] and the second is based on the alkylation of di- and tri-substituted amidines[102]:



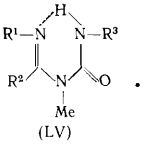
It is of interest that, when the trisubstituted amidines (LIV) are alkylated by the relatively unreactive alkyl halides, the alkylation may be accompanied by the abstraction of the elements of hydrogen halides from the alkyl halides to form the corresponding amidinium salts[101]:



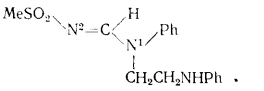
III. STRUCTURE AND PHYSICOCHEMICAL PROPERTIES

When the structure of amidines is considered, one must take into account the possibility of the prototropic "amidine" tautomerism due to proton transfer from one nitrogen atom to another. However, in many instances, it is possible to detect by physicochemical methods only one of the tautomeric forms. Thus it has been established by infrared spectroscopy for a series of cyclic amidines derived from 2-amino-Δ^1-piperideines that these compounds exist in the amino-form[103]. When there is an electron-accepting substituent at one of the nitrogen atoms, the tautomer in which the C=N bond is conjugated with this substituent usually predominates[75,95].

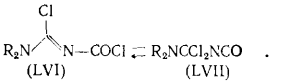
The study of the structure of *N*-carbamoylamidines (LV) by infrared spectroscopy made it possible to detect a strong intramolecular hydrogen bond in these compounds[104]:



The infrared spectra proved to be extremely useful also for the study of the hydrogen bonds between amidines and the solvent. Thus it has been established that formamidine derivatives form complexes of two types with chloroform: with participation of both the imino- and amino-nitrogen atoms[105], while in cyclic amidines[103] the hydrogen bond with $CHCl_3$ is formed only with participation of the ring nitrogen. Infrared spectra have also been used to elucidate the character of the coordination in boramidines[106]. The problem of the relative position of the substituents with respect to the C=N bond in amidines has attracted much attention. The *syn-anti* isomerisation in amidines of various types has been studied[107,108] by ^{1}H NMR. In the investigation of the addition of secondary amines to isonitriles[76,77] the authors concluded that *Z*-formamidines are formed initially and, being thermodynamically unstable, then rearrange to the *E*-isomers#. On the other hand, it has been stated[92] that stable *Z*- and *E*-isomeric *N*-sulphonylamidines have been isolated. However, subsequently, in a detailed study of their structures by infrared spectroscopic, ^{1}H NMR, and ^{13}C NMR methods, it was established that the substances isolated are rotational isomers relative to the C–N^1 bond[110]:



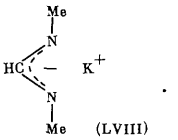
Interesting data have been obtained in a study[111] of the structure of *N*-chlorocarbonylchloroformamidines (LVI)—it was established that they are in equilibrium with the corresponding *N*,*N*-dialkylamino-1,1-dichloromethyl isocyanates (LVII):



A series of studies have been devoted to the hindered rotation relative to the C=N bond in amidines by ^{1}H NMR [108, 112–117]. The free energies of activation for the process ($\Delta G^{\neq}$) are usually not unduly high and, depending on the amidine structure, vary in the range 11–21 kcal mol^{-1}, the

#The assignment of amidines to the *Z*- or *E*-series can also be achieved by ^{13}C NMR.[109]

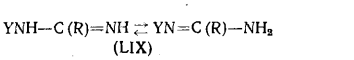
values for amidinium salts being appreciably higher[108]. It is of interest that the phenomenon of hindered rotation relative to the C=N bond could not be observed for the potassium salt of the amidine (LVIII):[112]



(LVIII)

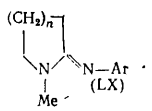
We may note that the "amidine" tautomerism was investigated in the same study by ^{1}H NMR and the thermodynamic parameters of the tautomeric equilibrium were obtained[112].

The position of the tautomeric equilibrium was estimated quantitatively by ultraviolet spectroscopy and by comparing the ionisation constants of certain amidines and model compounds[118,119]. It was shown that the equilibrium



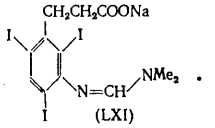
(LIX)

involving the amidines (LIX), where Y is an electron-accepting substituent, is significantly displaced to the right and that $K_T \cong 30$ for Y = acyl and $K_T \cong 10^7$ for Y = SO_2R.[118] If Y is a substituted phenyl group, the equilibrium is not displaced quite so much and $K_T = 2.4$.[119] The ionisation constants of a series of cyclic amidines have been measured[120–122] and it has been shown that the pK_a depend significantly on the ring size§ and that the basicity decreases in the sequence $C_6 > C_7 > C_8 \cong C_5$.[122] The authors explain this phenomenon by conformational factors—for the six-membered ring there is a possibility of a planar configuration of the amidine fragment, which is energetically unfavourable for the five-, seven-, and eight-membered compounds due to the non-bonding interactions of the protons in the ring methylene groups[122]. The study of the ionisation constants of a series of amidines and of the correlation between the pK_a and the σ constants[124,125] led the authors to the conclusion that the values of ρ and in general the basicity of the amidines depend to a greater extent on the substituents at the imino-nitrogen atom than on the substituents at the amino-atom. The study of the protonation of 2-arylimino-1-azacycloalkanes (LX) showed[126] that it involves the exocyclic, imino-nitrogen atom:



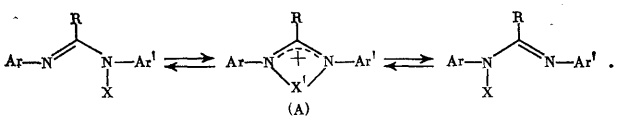
(LX)

The amidines (LX) are extremely strong bases (pK_a = 6.5–9.6), whose basicity also depends on the ring size[123,126]. On the basis of correlation analysis involving a comparison of the pK_a with the σ and σ^- constants, it was established in the above studies that the arene ring has been rotated relative to the C=N bond by approximately 50–60 °C. A similar rotation of the heteroaryl residue apparently occurs also in derivatives of *N*-(3-pyrazolyl)-amidines[44]. The high basicity of amidines is used in analytical chemistry for their quantitative analysis—one of the methods of analysis¶ of the radiocontrast agent bilimin (LXI) is its titration with $HClO_4$ in acetic acid[127]:



(LXI)

As already stated, the "amidine" tautomerism is due to proton transfer from one nitrogen atom of the triad to another. The 1,3-transfer of various groups within the amidine system, which has been studied by dynamic ^{1}H NMR [134–138] and by quantum-chemical calculations[139], is closely related to tautomerism of this type:



(A)

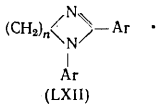
This reversible process has been studied for various substituents (X = acyl[134,138], 2,4-dinitrophenyl and picryl[135,138], or suphenyl[136,137]). Special experiments[134] estalbished that the 1,3-transfer process is intramolecular.

The energetic characteristics of the process depend on the structure of X and also on the structure of the substituents R, Ar, and Ar'. It is significant that the activation entropy $\Delta S^{\neq}$ for X = acyl is small and positive and that in such cases (A) is not a transition state but an intermediate. On the other hand, when X = SR^1, we have $\Delta S^{\neq} = -14$– -24 e.u., so that the transition state is more ordered than the ground state, which agrees with a structure of type (A). In the ^{1}H NMR studies of acyl- and sulphenyl-amidines at low temperatures, hindered rotation relative to the N–CO and N–S bonds respectively was observed.

IV. CHEMICAL PROPERTIES

1. Reactions With Nucleophiles and Electrophiles

The simplest reaction of amidines or their salts with nucleophiles is their hydrolysis. The mechanism of the hydrolysis of amidines was studied in detail in a monograph[1] and new investigations[121,122,140] did not introduce significant changes into the existing ideas. Examination of the question of the influence of ring size on the rate of alkaline hydrolysis of the cyclic amidines (LXII) [122,123] enabled the authors to establish the following sequence of decreasing rate constants: $C_5 > C_6 > C_7 > C_8$:[122]



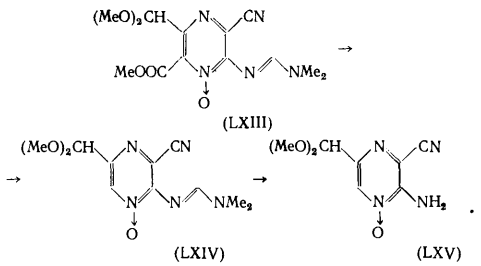
(LXII)

The authors attributed the highest rate of cleavage of compound (LXII, n = 2) to the strain in the five-membered ring, while the low rate of hydrolysis of seven- and eight-membered amidines is caused in their view by steric hindrance to the

§ For a review of the dependence of the properties of organic compounds on ring size, see Granik[123].

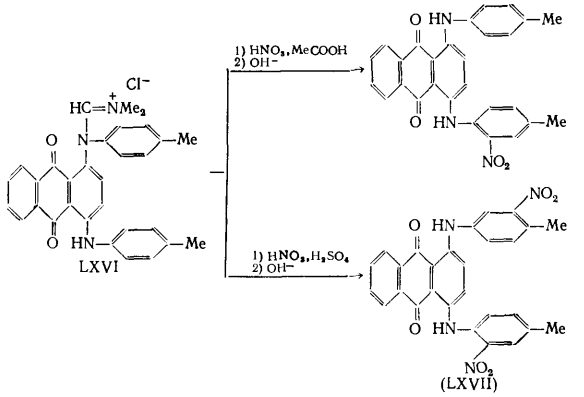
¶ In general amidines can be analysed quantitatively most effectively by titrating them as monoacidic bases. A study has been published recently[128], according to which certain amidines can also be analysed by gas–liquid chromatography (GLC).

attack by the hydroxide ion on these rings[122]. Comparison of the rates of the acid and alkaline hydrolysis of *N,N'*-dimethylformamidine showed that in an alkaline medium the process is significantly faster. An interesting study[41] of the conditions governing the retention and cleavage of the amidine group on hydrolysis as a function of the synthetic aim has been published recently. Thus it has been possible to hydrolyse selectively (and then decarboxylate) the methoxycarbonyl group of the substituted pyrazine (LXIII) without affecting the amidine group, by refluxing a solution of this compound in moist pyridine in the presence of lithium iodide. On the other hand, in the next stage it was necessary to remove selectively the formamidine group without involving the acetal group. The usual method, involving treatment with aqueous ammonia, proved to be unsuitable, since closure of the pyrimidine ring was observed under these conditions; acid hydrolysis in aqueous solution was also impossible owing to the dissociation of the acetal protecting group:



(LXIII) (LXIV) (LXV)

Taylor and Dumas[41] found an unexpected solution and obtained the amino-derivative (LXV) by keeping the formamidine (LXIV) in the 1:1 MeOH–$CH(OMe)_3$ mixture in the presence of $TsOH.H_2O$. In the case considered above, in order to protect the amino-group the latter was transformed into the formamidine group. This type of protection made it possible to solve the problem of the synthesis of mononitro- (or monobromo- and mono-*N*-acyl) derivatives of anthraquinone (LXVI):[141–143]



LXVI (LXVII)

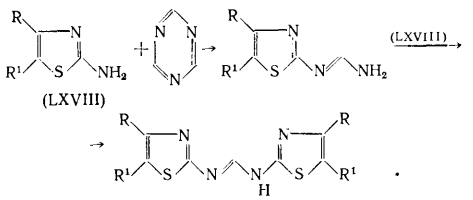
The use of an amidinium protecting group with its subsequent hydrolysis permitted the synthesis of derivatives of type (LXVII), which are extremely difficult to obtain by other methods and which have *o*- and *m*-substituents in the symmetrical aryl substituents in the 1,4-positions in the anthraquinone ring[141]. The hydrolysis of the amidine fragment was the concluding stage in a new synthesis of imides[49]:

$$RCON{=}C(R^1)NMe_2 \xrightarrow{H_2O(MeCOOH)} RCONHCOR^1 .$$

The discussion of investigations of this kind must be completed by stating that the hydrolysis of cyclic amidines is a model reaction for the investigation of the enzymic transfer of single-carbon components[144,145]. This problem has been reviewed[146]. One of the extremely important reactions of amidines or their salts with nucleophiles, which is used as one of the stages in heterocyclic synthesis (see below), is the transamination reaction. The synthesis of *N,N'*-disubstituted amidines by means of this reaction has been described recently[147]:

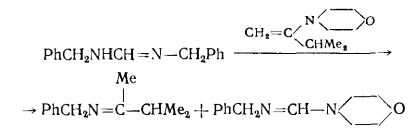
$$RC(=\overset{+}{N}H_2)NH_2Cl^- \xrightarrow{R^1NH_2} RC(=\overset{+}{N}HR^1)NH_2Cl^- \xrightarrow{R^1NH_2} RC(=\overset{+}{N}HR^1)NHR^1Cl^- .$$

The interaction of heterocyclic amines [for example, compound (LXVIII)] with *sym*-triazine is also accompanied by transamination[148]:

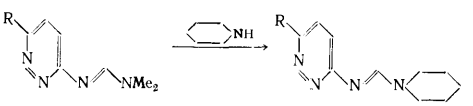


(LXVIII)

The reaction of amidines with tertiary enamines is extremely interesting—here too the final result is transamination[149]:



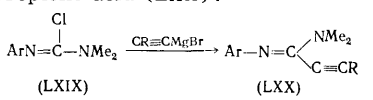
On heating, secondary amines are also capable of undergoing reactions of this type[150]:



The study of the properties of *N*-anthraquinonylformamidines showed that they react with nucleophiles only in the protonated form[151]. Studies of the transamination of enamidines established that, instead of involving the amidine meso-carbon atom, the reaction takes place at the enamine α-position with formation of enamines (and not pyrimidines as might have been expected)[152]:

$$Me_2N{-}CH{=}N{-}CH{=}C(CN)COOEt \xrightarrow{RR^1NH} RR^1N{-}CH{=}C(CN)COOEt$$

Substituted chloroformamidines readily react with nucleophiles, forming guanidines of various types[55,56,71], urea derivatives[70], and *O*-alkylisoureas[154]. The interaction of the amidines (LXIX) with ethylmagnesium bromide leads to amidines of propiolic acid (LXX):[155]

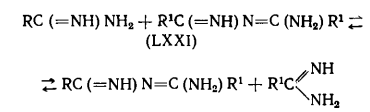


(LXIX) (LXX)

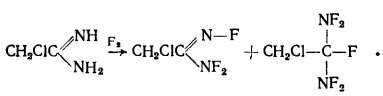
On treatment with sodium alkoxide at low temperatures, *N,N,N'*-trifluoroamidines yield a mixture of *N*-fluoroiminoesters and esters[156]:

$$RC(=NF)NF_2 \xrightarrow{EtONa,EtOH} RC(=NF)OEt + RCOOEt .$$

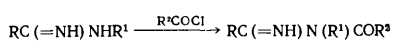
When amidines react with fairly strong C-acids, salts are formed[157]. The reaction is of first order with respect to both components. However, when the deutero-analogue of the C-acid instead of the C-acid itself is introduced into the reaction, complex kinetics, induced by numerous isotope exchange processes, are observed[157]. The exchange reactions involving imidoylamidines (LXXI) have been investigated by ^{19}F NMR,[158,159] for example:



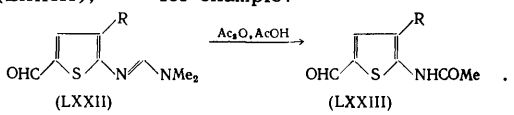
Among the reactions of amidines with electrophiles investigated in recent years, we may mention in the first place fluorination, which occurs mainly with formation of *N,N,N'*-trifluoro-derivatives[160], although in some cases products of the addition of fluorine to the C=N bond have also been isolated[160]:



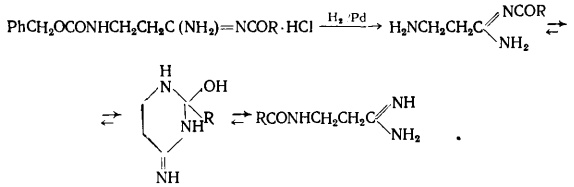
A series of investigations of the acylation of amidines have been made. *N*-Monosubstituted amidines are acylated by acyl chlorides at the substituted nitrogen atom[161]:



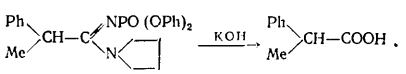
The acylation of *N*-heteroaryl-*N,N'*-dimethylformamidines (LXII) results in the formation of the corresonding acylamides (LXXIII),[42,162] for example:



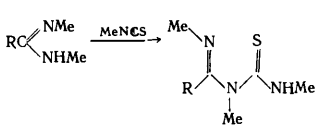
The acylation of compounds containing simultaneously the amino- and amidino-groups has been studied and an analytical method has been developed whereby it is possible to determine the position of the acyl group[163]. The observation[163] that the acyl group is transferred in acylaminoamidines is extremely interesting:



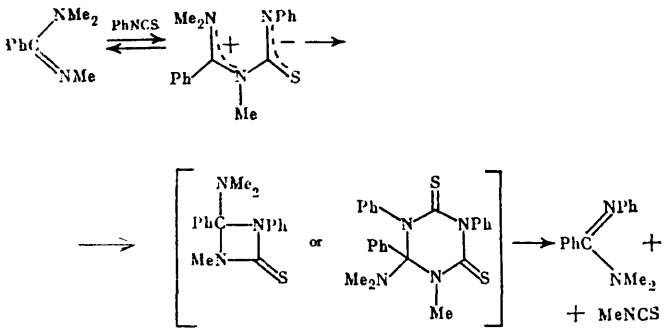
The acylation of *N*-dichlorophosphonylamidines by acyl chlorides takes place at the unsubstituted nitrogen atom[94]. Compounds substituted at a nitrogen atom by the $PO(OEt)_2$, PCl_3, and PCl_4 groups have also been synthesised by the reaction of amidines with triethyl phosphite[164] and phosphorus pentachloride[165,166]. Amidines substituted at a nitrogen atom by the phosphoric acid residue have served as starting materials in a new synthesis of substituted acetic acids[167]:



The interaction of amidines with alkyl isothiocyanates results in the formation of *N*-thiocarbamoylamidines[168,169]:



On the other hand, the exchange reaction



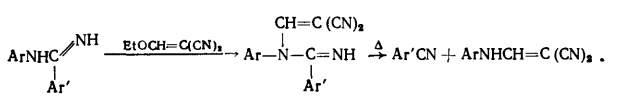
takes place when *N,N,N'*-trisubstituted amidines interact with aryl isothiocyanates[170]. The hypothesis of stringent steric requirements which must be met by the transition state is confirmed by the high negative entropy of activation (−36.1 e.u.).[170]

The study of the synthesis of fluorinated imidoylamidines by the reaction of amidines with nitriles is closely related to the above investigations[171]:

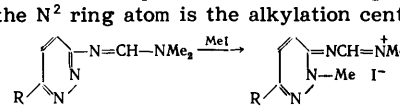


where R_F and R_F^1 are fluorinated groups. It is noteworthy that this reaction is extremely sensitive to the steric factor and that its rate decreases sharply with increase in the bulk of R_F^1.[171]

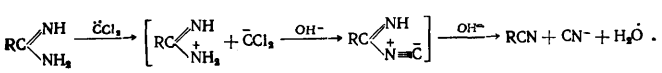
In a few studies of the alkylation of amidines having the NH group it has been shown that the reaction usually proceeds fairly smoothly. This is observed in the interaction of amidines with propiolic acid ester[172], alkyl halides[173] (in the latter case lithium salts of amidines have also been used), and ethoxymethylenemalononitrile[172,174]. We may note that the enamidines thus formed are cleaved to enamines and nitriles on heating[174]:



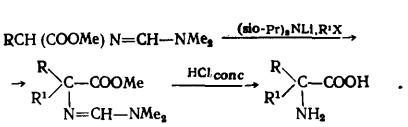
The alkylation of *N,N*-dimethyl-*N'*-(3-pyridazinyl)formamidine by methyl iodide takes place in an interesting manner—in this case the N^2 ring atom is the alkylation centre[150]:



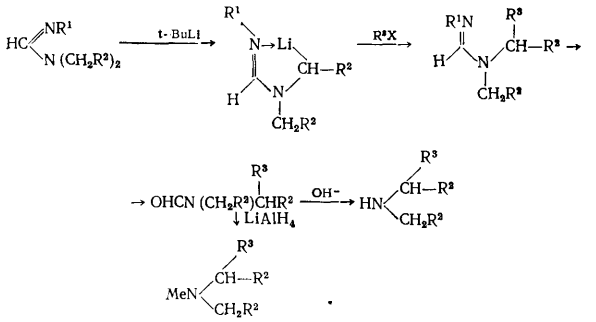
Dichlorocarbene also attacks amidines at the unsubstituted nitrogen atom—the final result of the reaction (appearing under the conditions of phase-transfer catalysis) is a nitrile and a cyanide ion[175]:



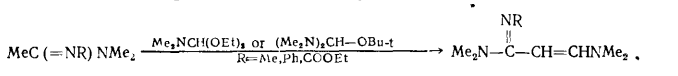
A new method of synthesis of α-substituted aminoacids based on the alkylation of *N,N,N'*-trisubstituted amidines has been published recently[45]:



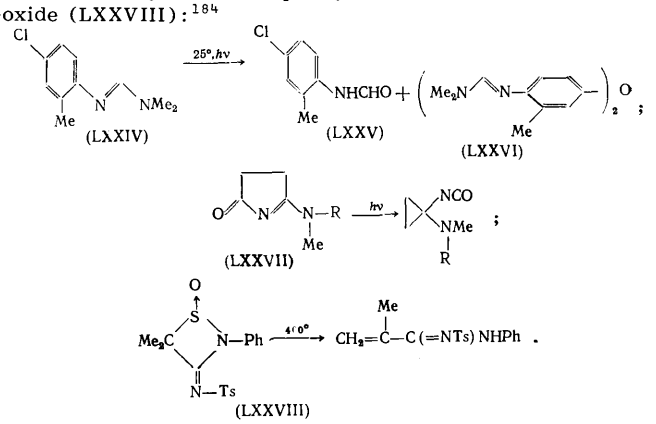
A new method of synthesis of α-substituted amines is also based on an analogous principle[176]:



In the studies of the reactions of amidines with electrophiles discussed above, the process involved either a nitrogen atom or a carbon atom of an alkyl group attached to a nitrogen atom. The possibility of the substitution of the protons of the methyl (methylene) group attached to the amidine meso-carbon atom† follows from a comparison of the electron-accepting influences of the iminoester and amidine functional groups[177]. The ability of amidines of type (LX) (see Section III above) to react with electrophiles at the α-$CH_3(CH_2)$ groups was first demonstrated in relation to the deuterium exchange reaction[177]. It was established that compounds (LX) exchange the ring α-protons for deuterons under mild conditions (CD_3OD, 20 °C) and that the exchange is accelerated in the presence of acid and basic catalysts[177]. The ring α-protons of enamidines (XXXI) (see Section II above) are also exchanged for deuterium albeit under more severe conditions[60]. A series of studies demonstrating that amide acetals and aminal-esters are capable of condensing via the methyl (methylene) group attached to the amidine meso-carbon atom have been published recently[46,52]:



In conclusion of this section, we may point to studies of the photolysis of *N*-(*p*-chloro-*o*-methylphenyl)-*N'*,*N'*-dimethylformamidine (LXXIV), which is converted into the corresponding formyl derivative (LXXV) and the bisamidinoester (LXXVI) on ultraviolet irradiation in water[182], the photochemical rearrangement of the cyclic amidine (LXXVII),[183] and the thermolysis of 3-sulphonylimino-1,2-thiazetidine 1-oxide (LXXVIII):[184]

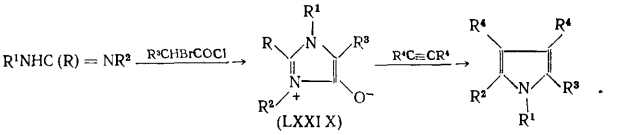


†This principle of the introduction of substituents into the α-$CH_3(CH_2)$ group, called the "principle of potential enaminisation", was also used in the study of the reactions of amide and lactam acetals and also various types of enamines with electrophiles and proved to be the most effective when applied in heterocyclic synthesis (see, for example, Refs.178–181).

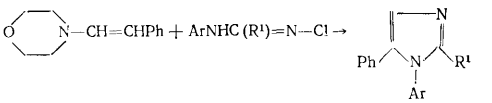
2. Heterocyclisation Reactions

The synthesis of heterocycles using amidines is also based on their reactions with electrophiles or nucleophiles. However, bearing in mind the importance of this field of study, we thought it useful to consider the heterocyclisation reactions separately in their own section of the review.

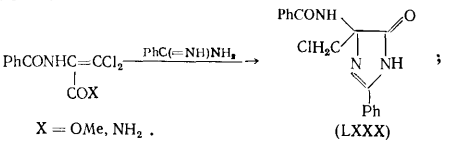
Amidines have been the starting materials for the synthesis of a large group of five-membered heterocycles. Thus 2-dialkylamidino-2,4,5-triphenyl-2,3-dihydro-3-pyrrolones have been synthesised by the reaction of *N*,*N*-dialkylbenzamidines with diphenylcyclopropenone[185]. A number of studies have been made on the synthesis of the mesoionic compounds (LXXIX), which are converted into pyrroles on treatment with acetylenic derivatives[186–188]:



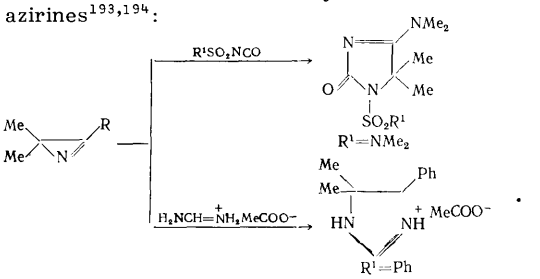
When tertiary enamines react with *N*-chloroamidines, imidazole derivatives are formed[189–191]:



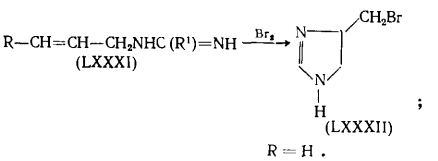
The imidazolones (LXXX) have been obtained by the reaction of α-carbamoyl (or ethoxycarbonyl)-β,β-dichloroenamides with amidines[192]:



Imidazole derivatives have also been synthesised from substituted azirines[193,194]:

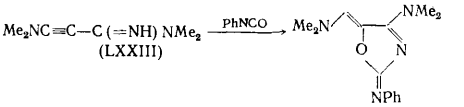


It has been established recently that the amidines (LXXXI), having an unsaturated group in the side chain, can be converted into the imidazolines (LXXXII):[195]

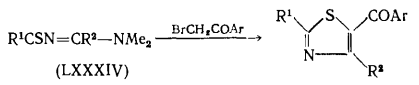


We may note that, when R = Ph in compound (LXXXI), tetrahydropyrimidine derivatives are formed[195].

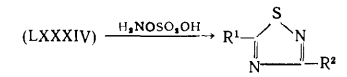
The reaction of ynaminoamidines (LXXXIII) with carbon dioxide or phenyl isocyanate has been used to synthesise oxazole derivatives[53]:



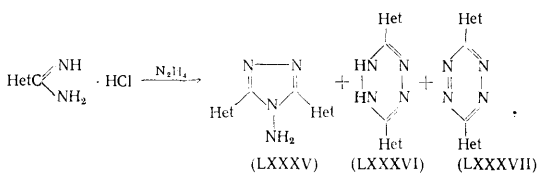
A preparatively convenient method of synthesis of substituted thiazoles is based on the reaction of thioacylamidines (LXXXIV) with α-bromoketones[196,197]:



The amidines (LXXXIV) are also used to synthesise thiadiazoles[48]:



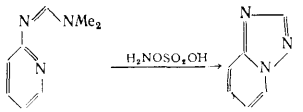
The same principle has been applied in the synthesis of triazole[47,52] and oxadiazole[47] derivatives: in these cases *N*-acylamidines[47] or *N*-ethoxycarbonylamidines[52] were made to react with hydrazine[47,52] and hydroxylamine[47]. An interesting synthesis of *N*-aminotetrazoles (LXXXV) and the tetrazines (LXXXVI) and (LXXXVII) is based on the interaction of heteroarylamidines with hydrazine[198]:



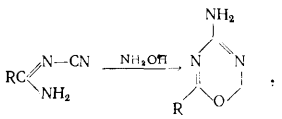
(LXXXV) (LXXXVI) (LXXXVII)

where Het = 2-furyl, 2-thienyl, 3-furyl, 3-thienyl, 2-selenophenyl, or 3-selenophenyl.

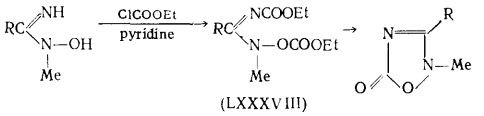
A new synthesis of condensed triazoles from *N*-(2-pyridyl)- and *N*-(1-isoquinolinyl)-formamidines has been published recently[199]:



N-Hydroxy- and *N*-cyano-amidines have been used in the synthesis of oxadiazoles[200]: in the former case amidines are made to react with bromocyanogen or trichloroacetic anhydride and in the latter with hydroxylamine:

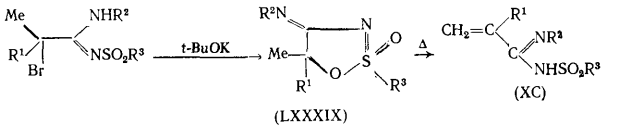


Another method of synthesis of oxadiazoles from *N*-hydroxyamidines consists in their interaction with chlorocarbonic ester and subsequent intramolecular cyclisation of the intermediate *O*,*N*-bisacyl derivative (LXXXVIII):[201]



(LXXXVIII)

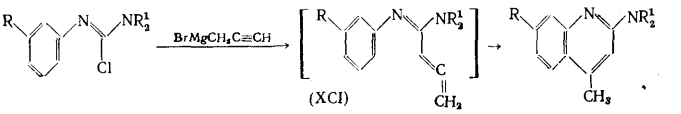
The conversion of α-bromo-*N*-sulphonylamidines into oxaisothiazolines (LXXXIX), which isomerise on heating to the enamidines (XC), has also been described[202]:



(LXXXIX) (XC)

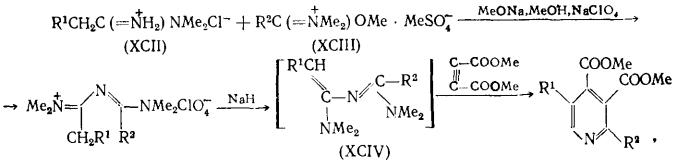
The employment of amidines in the synthesis of various six-membered, particularly pyridine, pyrimidine, and triazine, systems is even more promising.

The closure of the pyridine ring was achieved on reaction of chloroformamidines with ethynylmagnesium bromide or propargylmagnesium bromide[155]. In the latter case the process apparently proceeds via the intermediate formation of the allene (XCI):



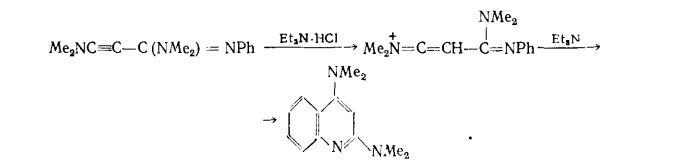
(XCI)

The reaction of the amidine salt (XCII) with the methyl sulphate complex (XCIII), followed by treatment of the intermediate enaminoamidine (XCIV) with acetylenedicarboxylic ester, also leads to the formation of a pyridine derivative[203]:

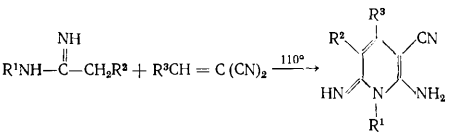


(XCII) (XCIII) (XCIV)

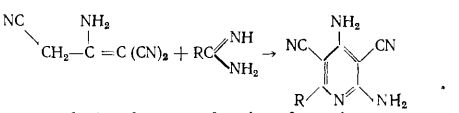
It has likewise been shown that the presence of the triple bond in the substituent at the meso-carbon atom of the amidine also makes it possible to achieve intramolecular cyclisation with formation of quinoline derivatives[204]:



A number of studies have been devoted to the synthesis of pyridines by the reactions of amidines with ylidenemalononitriles[205,206]:

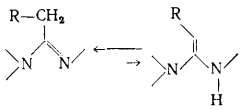


A reaction of a similar type also takes place between formamidine or acetamidine and the malononitrile dimer—in this case tetra- or penta-substituted pyridines are also formed[42]:

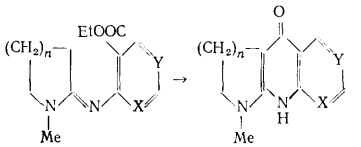


Another approach to the synthesis of various types of pyridine-containing heterocycles is based on the principle of potential "enaminisation" mentioned above (Section IV, subsection 1). The significance of this principle consists in the fact that the protons of the $CH_2(CH_3)$ groups attached to the amidine *meso*-carbon atom are fairly acidic and under certain conditions can be split off, creating thereby the basis for electrophilic substitution, for example, for deuterium exchange (see Section IV, subsection 1) or intramolecular cyclisations. There is then a possibility of the intermediate formation of enamines, although their appearance has not been detected experimentally#:

#In the study of the synthesis of pyridazines, definite evidence has been obtained quite recently in support of the occurrence of such amidine–enediamine tautomeric equilibrium (see below).

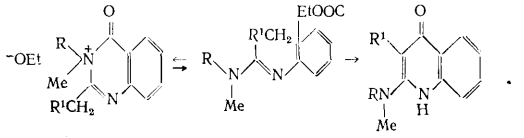


A number of syntheses of 4-pyridones, 4-quinolones and derivatives of pyrrolo-, pyrido-, and azepino-quinolines, pyrrolo-, pyrido-, and azepino-naphthyridines, and pyrrolo-, pyrido-, and azepino-pyrido[2,3-*d*]pyrimidines have been achieved using this approach[60,207-212]:

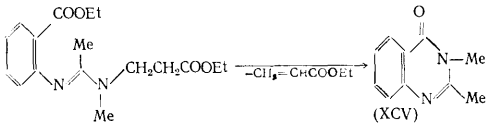


X=Y=CH; X=N, Y=CH, X=Y=N.

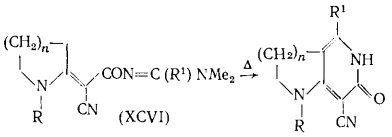
Reversible cyclisation at a nitrogen atom of the amidine system apparently takes place initially and the equilibrium is then displaced to the right as a result of the irreversible formation of a pyridone:



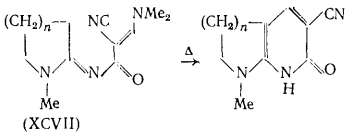
This hypothesis has been confirmed by the observation[209] that, when the substituent R can be split off in the form of a stable molecule, the only reaction product formed is a quinazolone derivative (XCV):[209]



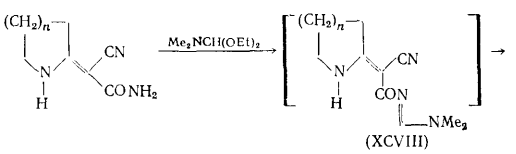
Enaminoacylamidines (XCVI) and (XCVII) proved to be an extremely promising class of compounds for the synthesis of various condensed pyridines[213-218]:

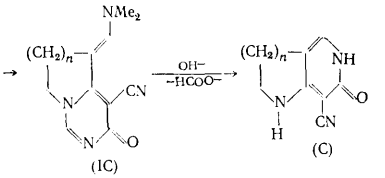


R=Me, $PhCH_2$, R¹=H, Me

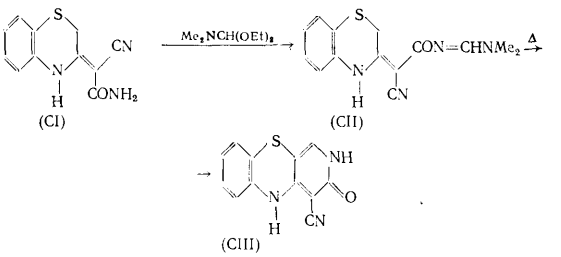


A study of the kinetics of both types of reaction showed that the rate of cyclisation is many times higher for compounds (XCVI) than for compounds (XCVII),[216] which corresponds to a more effective delocalisation of the positive charge in the amidine system compared with the enamine system. Enaminoacylamidines (XCVIII) are intermediates also in a new pyrimidine synthesis[215,217,219-223]:

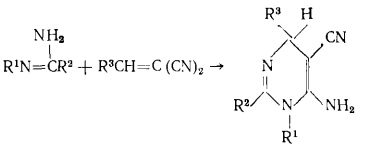




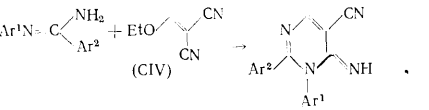
It is of interest that condensed pyrimidines (XCIV) behave similarly to cyclic amidines (see Section IV, subsection 1) and readily hydrolyse in an alkaline medium with elimination of formic acid[219,220] and recyclisation to 2-pyridone derivatives (C).[217,219-222] When the enaminoamide (CI) obtained from 2-benzothiazinone was used in the reaction, it was found that the intermediate acylamidine (CII) cyclises on heating to pyridobenzothiazine (CIII) and not to a pyrimidine derivative[223]:



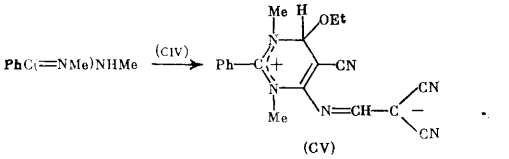
Pyrimidine derivatives are formed smoothly on interaction of amidines with various three-carbon components, such as dicarbonyl[224] and enaminocarbonyl[225,226] compounds as well as acetylenedicarboxylic ester[64]. Substituted pyrimidines are also formed when amidines react with various derivatives of 4-benzopyrone[227-229] or pyrylium salts[230]§. The reaction of amidines with ylidenemalononitriles leads to dihydropyrimidines[232,233]:



It has been shown[174] that the reaction of amidines having a primary amino-group with ethoxymethylenemalononitrile (CIV) takes place in the usual manner with formation of 4-iminopyrimidines:



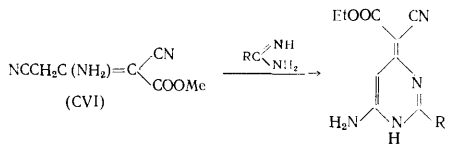
However, compound (CIV) reacts differently with *N*,*N'*-disubstituted amidines and the reaction product is in this case the zwitterionic 1:2 adduct (CV):[172]



(CV)

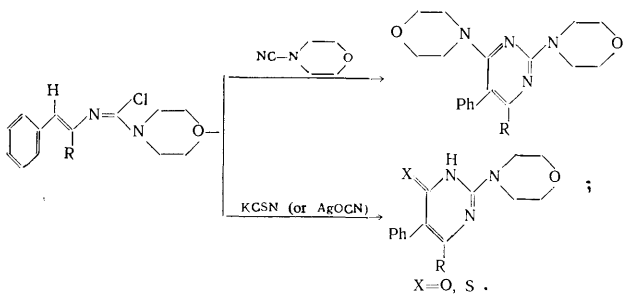
§ For a review of the transformations of oxygen-containing rings into pyrimidines under the influence of amidines (and guanidines), see Takagi and Hubert-Hebart[231].

The interaction of the codimer of malononitrile and cyanoacetic ester (CVI) with benzamidines and acetamidines (but not with formamidine—pyridines are formed in this instance) leads to derivatives of 4-methylenepyrimidine (CVII):[42]



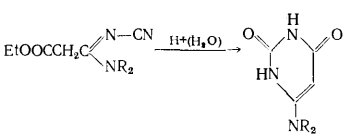
(CVI) (CVII)

Substituted chloroformamidines can be used successfully to synthesise substituted pyrimidine derivatives[234]. For this purpose, they are made to react with derivatives of cyanamide, silver isocyanate, or potassium isothiocyanate:

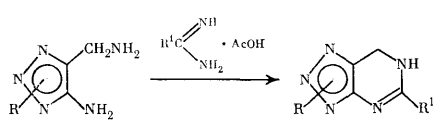


X=O, S.

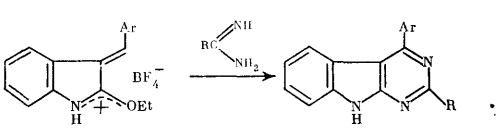
The salts of enaminoamidines can also serve as a source of pyrimidines, both directly (via their reaction with amidines[6]) and after their conversion into enaminoamidines of type (XCIV) (see above) followed by treatment with phenyl isothiocyanate[203]. A new synthesis of pyrimidine-2,4-diones by the intramolecular cyclisation of *N*-cyanoamidines has been published recently[235]:



Certain amidines have been used recently[236] as single-carbon components in the synthesis of condensed pyrimidines:

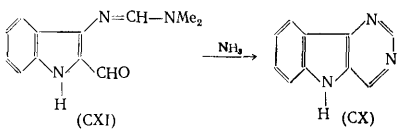


The presence of the amidine and carbamide functional groups in neighbouring positions ensures the possibility of the closure of the pyrimidine ring on interaction with formamide[237]. Pyrimidoindoles (CVIII) have been synthesised successfully by the reaction of amidines with tetrafluoroborate complexes (CIX):[238,239]



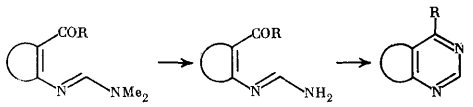
(CIX) (CVIII)

Pyrimidoindoles of another type (CX) have been synthesised by the reaction of the indolylamidine (CXI) with ammonia, primary amines, and hydroxylamine[240], for example:

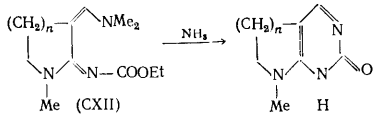


(CXI) (CX)

The first stage in pyrimidine synthesis of this type is usually transamination with subsequent cyclisation involving the participation of the adjacent carbonyl-containing group:

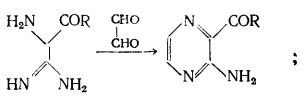


Anthrapyrimidines[151], pyrazolopyrimidines[152], and pyridopyrimidines[211] have been obtained by this method. A new synthesis of pyrimidines and derivatives of pyrrolo-, pyrido-, and azepino-[2,3-*d*]pyrimidines is based on the reaction of enaminoamidines of type (CXII) with ammonia[52]:



Me (CXII) Me H

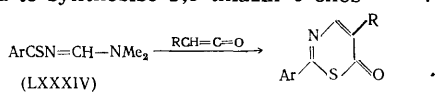
The aminoamidines (CXIII) have proved to be convenient starting materials for the synthesis of 2-amino-3-ethoxycarbonylpyrazines—important intermediates in the synthesis of pteridines[241,242].



(CXIII)

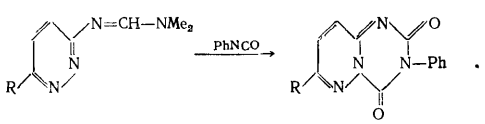
R=OEt, NH_2.

The *N*-thioacylamidines (LXXXIV) already mentioned above have been used to synthesise 1,3-thiazin-6-ones[197,243]:

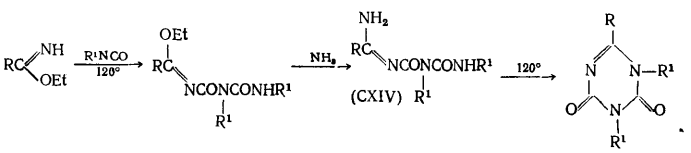


(LXXXIV)

Numerous studies have been devoted to the synthesis of triazine derivatives from amidines. The main bulk of these syntheses are associated with the use of various isocyanates and isothiocyanates, for example, phenyl isocyanates, as the second reaction component[150,244]—in these cases *N*-heteroarylamidines were introduced into the reaction:

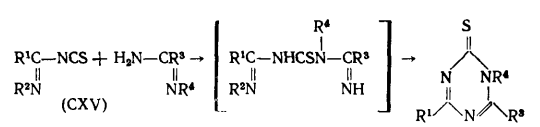


[1,2]-Adducts (triazinediones or triazinedithiones) are also formed when amidines react with benzenesulphonyl isocyanate[168] or methyl isothiocyanate[168,169]. The study of the synthesis of triazine derivatives by the intramolecular cyclisation of the amidine (CXIV), obtained by treating the corresponding iminoester with R^1CNO and then with ammonia[245], is related to these investigations:



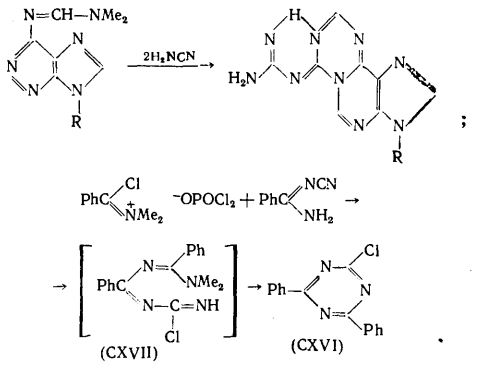
(CXIV)

sym-Triazinethiones have also been obtained by the reaction of iminoisothiocyanates (CXV) with amidines[246,247]:



(CXV)

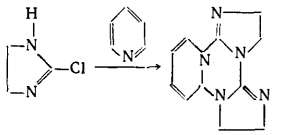
The reactions of amidines with cyanamide[43] and the reaction of *N*-cyanoamidines and complexes of amides with phosphoryl chloride[248] belong to another class of methods of synthesis of triazines:



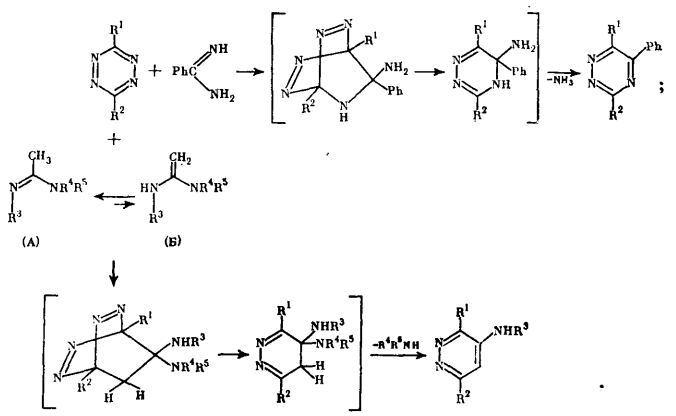
(CXVII) (CXVI)

The author does not explain why chlorotriazine (CXVI) is formed, but one can suppose that the intermediate chloroimide (CXVII) cyclises.

The triazine ring is also formed in the reaction of cyclic chloroformamidines with pyridine or quinoline[249]:

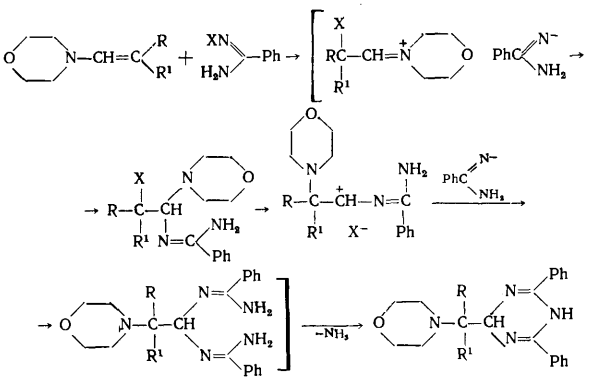


Amidines behave as dienophiles in reactions with tetrazines, which result in the formation of 1,2,4-triazines[250]. It is significant that, when *N*,*N*,*N'*-trisubstituted amidines are made to undergo an analogous reaction, pyridazines are produced[251]. The authors believe that this process is a consequence of the amidine–enediamine equilibrium (A ⇌ B) [215] (see also above):

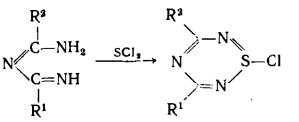


(A) (Б)

Finally we may note the interesting reaction of *N*-halogenoamidines with enamines via the mechanism[252]



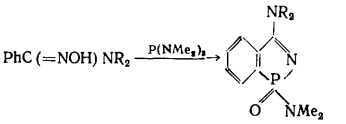
The 1,2,4,6-thiatriazine derivative (CXVIII) has been obtained by the reaction of imidoylamidines with sulphur dichloride[253]:



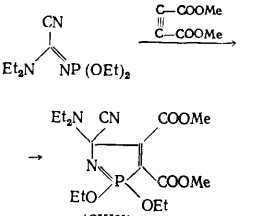
(CXVIII)

If *N*-arylamidines are introduced into a reaction of this kind, derivatives of 4-chloro-4-thiaquinazolines are formed[254].

In conclusion of this section, we may note studies devoted to the synthesis of phosphorus- and boron-containing heterocycles. The largest number of such studies have been made on phosphatriazines, which have been obtained by the reaction of *N*-cyanoamidines[255] or *N*-imidoylamidines[256] with phosphorus pentachloride, of trichlorophosphazo-compounds with amidines or *N*-dichlorophosphonylamidines[94], and also of *N*-hydroxyamidines with phosphines[257]. The last reaction involves *N*-hydroxyamidines unsubstituted at the second nitrogen atom. The reaction of the *N*-substituted compounds proceeds differently and a five-membered and not six-membered ring is formed[257]:

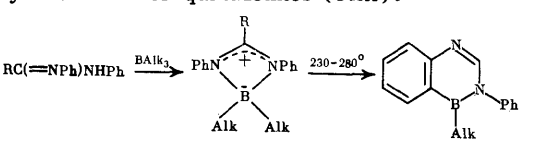


Phosphorus-containing amidines have been used in the synthesis of derivatives of azaphospholes (CXIX):[166]



(CXIX)

Since the review mentioned above[7] was devoted to boramidines, we shall mention only one recently published study on the synthesis of boraquinazolines (CXX):[258]



(CXX)

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This review has dealt with the literature data on the chemistry of amidines and was not concerned with the results of studies on related systems, such as those comprising derivatives of guanidine, *O*- and *S*-substituted ureas, and thioureas. Only in a few instances does the review deal with the chemistry of amidinium salts, because a series of recently published reviews have described their properties[6,259]. Examination of data on the above types of compounds together with those on the chemistry of amidines is hardly possible within the framework of a single article.

Summarising the literature data, one may claim that the development of the chemistry of amidines has been responsible for the development of various fields of organic chemistry, in the first place the chemistry of heterocycles, and has proved extremely fruitful in both theoretical and practical respects.

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Electronic Structure and the Chemical Bond in Non-stoichiometric Refractory Compounds of Transition Metals in Sub-groups IVa and Va

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Studies of the electronic structure and of the chemical bond in non-stoichiometric binary compounds based on the transition metals of sub-groups IVa and Va are systematically reviewed. The main phenomenological models are examined, and the results of calculations by band and by cluster models of the distribution of electron density are compared; changes in the chemical bond caused by the presence of point vacancies in the metalloid and in the metal sub-lattice are discussed. Calculated results are compared with the results of studies of non-stoichiometric compounds by X-ray emission and photoelectron spectroscopy methods, and with various physicochemical properties. The relative merits of the two approaches (using band and cluster models respectively) in studies of electronic processes associated with the formation of point vacancies in crystals are discussed. 159 references.

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I. INTRODUCTION

Compounds of the transiton metals (TM) of sub-groups IVa and Va of the Periodic Table with the lighter s and p elements (carbon, nitrogen, oxygen) form a large class of substances with a number of unique physicochemical properties. They combine properties typical of covalently bonded crystals (high melting point, superior hardness, resistence to corrosion and radiation) with specific properties of electrical and thermal conduction, magnetism, and superconductivity[1-10].

The most striking feature of the monocarbides, mononitrides, and monoxides of the TM is their extensive homogeneity region, which allows the concentration of defects (point vacancies) in both sub-lattices to be varied by large amounts

without disrupting the original structure (type B1). Even in stoichiometric compositions the number of vacancies can be 15–25 at.%, increasing rapidly as the composition departs from the equi-atomic ratio: some compounds (for example, vanadium carbide) cannot be prepared in a strictly stoichiometric state under normal conditions. Furthermore in some binary compounds (VO_x, TiO_x, VC_x, etc.) the defects are partially ordered, with formation of defect clusters, and this can lead to the appearance of individual phases like V_6C_5, V_8C_7, $VO_{1.3}$, etc.[1-10]

Deviations from stoichiometry produce large changes in all the physicochemical properties of the compounds. Therefore the wide interest in the electronic structure of non-stoichiometric phases and in the electronic processes which accompany the formation of point vacancies in the crystal is not surprising.

A correct description of the electronic structure of non-stoichiometric phases (as opposed to that of an ideal crystal) should account for changes in the following properties: 1) the density of electronic states, 2) the position of the Fermi level, 3) the chemical bond near a defect. It should also correctly identify: 1) the nature of the vacancy states, their position in the overall energy spectrum, and the extent to which they are localised, and 2) the charge on the vacancies.

In this paper we shall attempt a systematic review of existing models of the electronic structure of MX_x binary compounds containing defects (where M is the metal and X is the non-metal), whether phenomenological or based on quantitative quantum-chemical calculations. We shall examine the relative merits of the different methods and approximations which have been used to describe the energy spectrum of electrons in the chemical bond of compounds with or without defects, and we shall compare them with data on MX_x compounds obtained by X-ray emission and photoelectron spectroscopy methods.

II. BAND AND CLUSTER MODELS USED IN THE CALCULATIONS OF THE ELECTRONIC STRUCTURE OF SOLIDS

Two alternative approaches to the calculation of the electronic structure of condensed phases are used at present: the band model and the cluster model. Both are based on the solution of the one-electron Schroedinger equation

$$\left\{-\frac{1}{2}\nabla^2 + V_{\text{coul}}(\mathbf{r}) + V_{\text{exch}}(\mathbf{r})\right\}\psi_j(\mathbf{r}) = \varepsilon_j\psi_j(\mathbf{r}) \qquad (1)$$

(where ∇^2 is the kinetic energy operator, $V_{\text{coul}}(\mathbf{r})$ is the coulombic potential energy of the electron, and $V_{\text{exch}}(\mathbf{r})$ is the exchange–correlation pontential), but they rely on radically different approximations.

In the energy band methods[11] special attention is paid to the properties of the energy spectrum arising from the presence of translational symmetry: the solid is treated as an infinitely large regular crystal. The wave function ψ_j is expressed as a combination of delocalised periodic functions of the Bloch type, and the electronic spectrum calculated in this way has continuous energy bands corresponding to the ground state of the ideal (defect-free) crystal, This approach is therefore useful for compounds which form bands (of any width), and it gives accurate values of the width and energy of the band. The characteristics which the band methods describe most correctly are those associated with delocalised electronic states (i.e. the kinetic properties).

The most serious weakness of this approach is that any deviation from the ideal crystal model (such as surfaces, impurities, defects, excited states, etc., which are found in the vast majority of real solids) will perturb the translational periodicity of the system and cause difficulties in the calculation of the energy bands in the disordered system.

Conversely, the molecular orbital cluster methods[12-14] describe the electronic structure as a set of discrete levels of energy ε_j, obtained by solving Eqn.(1) for a relatively small group of atoms (the cluster) chosen within the crystal. These methods retain the atomic orbital concept and rely on fairly simple computation schemes which are however applicable to compounds with crystal structures and compositions of any degree of complexity. Therefore the cluster methods are used mainly in calculations of electronic states and chemical bond effects in disordered solids containing defects, impurities, dislocations, etc. Cluster methods are most successful when applied to narrow-band crystals, and the most accurate results are obtained in calculations of characteristics associated with localised states.

One of the main shortcomings of the cluster approach is the difficulty of calculating kinetic parameters, and of describing wide-band systems.

Several independent methods are now available for band calculations (combined plane wave (CPW), orthogonalised plane wave (OPW), Green function, pseudo-potential methods, etc.) and for cluster calculations [semi-empirical or *ab initio* SCF MO LCAO methods, X_α-scattered wave (X_α-SW) methods, X_α-discrete variation (X_α-DV) methods, X_α-LCAO methods, etc.]. Since approximations have to be used even in non-empirical methods, and their validity may be doubtful, experimental tests of the results may be necessary. The most direct tests rely on X-ray emission and photoelectron spectroscopy. We shall therefore discuss the results of specific calculations in conjunction with relevant spectroscopic data in order to assess the validity of different models of the electronic structure of high-melting phases.

Before proceeding to our discussion of the electron energy spectrum (EES) of non-stoichiometric compounds we shall briefly examine the most important results relating to "complete" (i.e. ideal) binary phases, since these phases will be used later as reference systems when considering changes in electronic structure brought about by structural vacancies.

III. ELECTRONIC STRUCTURE AND THE CHEMICAL BOND IN STOICHIOMETRIC BINARY COMPOUNDS OF THE TRANSITION METALS

The earliest views on the electronic structure of high-melting compounds were formulated as two phenomenological models, each supported by a number of experimental facts[3,5,7-9]. According to the first of these models[15,16] interstitial phases can be treated as solid solutions of the metalloid in a matrix of the metal, where the main effects of chemical bonding arise from the collectivisation of the *d* electrons from the metal. The other model accounts for the hardness, refractoriness, and brittleness of these compounds by postulating a predominant contribution from covalent interactions between the metal and the metalloid[17-20].

The real structure of the EES of binary phases and the individual features of the electronic structure of particular compounds were successfully established by quantitative quantum-chemical calculations. Almost all the existing band and cluster methods have been applied to the calculation of the band structure of ideal binary compounds. The most important of these calculations are summarised in Table 1, which lists the methods applied to different materials and all the reported X-ray emission and photoelectron spectroscopy studies of these compounds.

Table 1. Bibliography of quantum-chemical calculations and X-ray emission (XE) and photoelectron spectroscopy (XPS) work on binary stoichiometric high-melting phases.

Compound	Band calculations				Cluster calculations		XE spectra	XPS spectra
	strong bond	CPW	Green function	empirical pseudo-potential	semi-empirical	$X\alpha$		
TiC	[21, 23, 26, 27, 53, 54]	[24, 34—37, 45—48]	—	[28, 29]	[67, 68, 70]	[57, 58, 60, 64, 65]	[77, 80—82, 84]	[34, 89]
TiN	[21, 53, 54]	[24, 35—37, 46]	—	—	[67, 70]	[60, 64]	[77, 78, 81, 82, 101, 158]	[92, 94, 95]
TiO	[21]	[24, 33, 35—37, 46]	—	—	[70]	[60, 64]	[77, 81—84]	[99]
VC	[26, 27, 53]	[34—40]	—	—	[67—69]	[59, 60, 64]	[80, 84, 85]	[34, 90]
VN	—	[35—39]	—	—	[67—69]	[59, 60, 64]	[78, 80, 85]	[96]
VO	—	[33, 35—37]	—	—	[69]	[60, 64]	[80, 85]	[100]
ZrC	[26, 27]	[34]	—	[29]	[62]	[58, 62]	[78, 79, 84]	[34]
ZrN	—	—	—	—	[62]	[62]	[78, 79]	—
«ZrO»	—	—	—	—	[62]	[62]	—	—
NbC	[26, 27]	[34, 42—44]	—	[30]	[71]	[61]	[79, 84, 86—88, 98]	[34, 89, 97]
NbN	[32]	[41, 43]	—	[30, 31]	[71]	[61]	[79, 86—88, 158]	[97]
NbO						[61, 66]	[66, 87, 88]	[66]
HfC	[26, 27]	[34, 49, 50, 52]	[55]	—	—	[63]	[84]	[34]
HfN	—	—	[56]	—	—	[63]	—	—
TaC	[26, 27]	[34, 49, 50, 52]	[55]	—	—	[63]	[84]	[34]
TaN	—	[51]	[56]	—	—	[63]	—	—

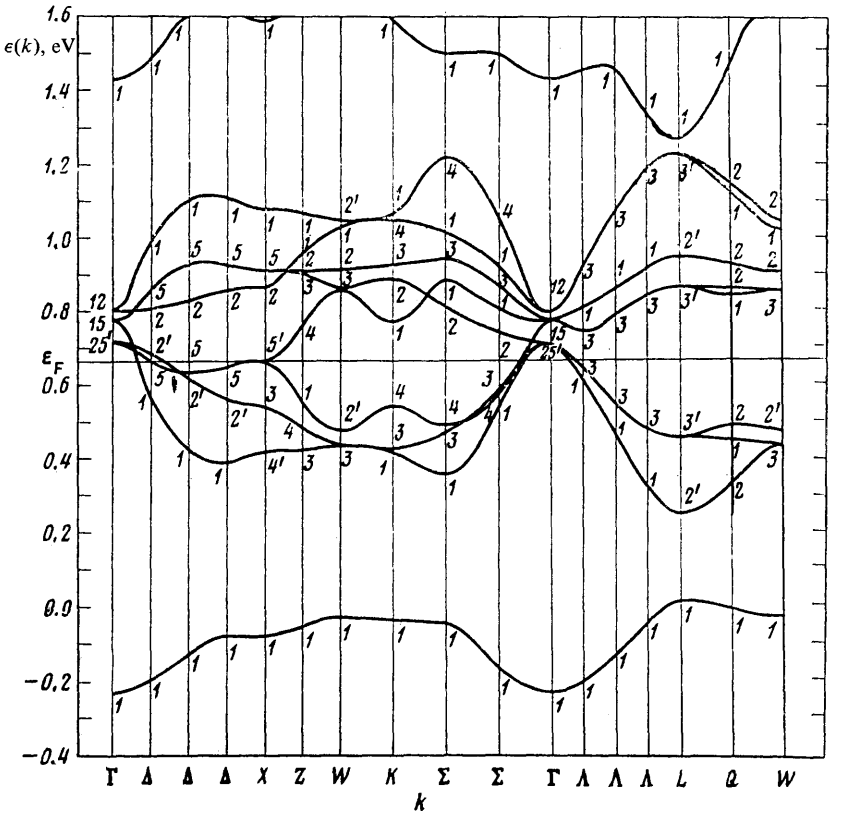


Figure 1. Band structure of titanium carbide (CPW calculation[36]).

The first calculation by Bilz[21] for TiC, TiN, and TiO by the strong bond method showed that the valence band of MX contains two sub-bands in which both M–X and M–M bonding can occur. However, the approximations used in that work[21] (such as the evaluation of two-centre integrals from data for the pure metals) led to some "averaging out" of the resulting band structure: this property was later put to use in the "quasi-rigid" band model, in which the general shape of the bands of the carbides, nitrides, and oxides of the *d* metals is assumed to be constant and only differences in the occupancy

of the energy bands (due to differences in the concentration of valence electrons between the different compounds) are considered.

Costa and Conte[22] confined their calculation for TiC to the *d* functions of the metal, which are split into t_{2g} and e_g components in the crystal field. They found that the M–M bond was stronger than in the pure metal, but their neglect of the Ti–C and C–C interactions makes this conclusion doubtful. This was pointed out by Lye and Logothetis[23], who evaluated the exchange integrals from spectroscopic data. In their band structure for TiC the e_g state of Ti was lower in energy than in the pure metal, giving a broad band of Ti–C interactions. This configuration of the bands should lead to high bond energies and to a melting point higher than that of titanium.

Conversely, in CPW calculations[24] for TiC, TiN, and TiO a transfer of charge in the opposite direction is obtained. The valence band is formed from the $2p(X)$ and the $3d$(Ti) states, and the Fermi level of TiC is found in a region of low density of electronic states $N(\varepsilon)$. As the atomic number z of the metalloid increases, the additional electrons populate the t_{2g} states in the metal, thus raising the level of ε_F. These results[24] were confirmed by an independent report[25] that charge (less than 1 electron) is transferred in the Ti → C direction.

Most of the calculations on binary MX phases were published during the 1970's and 1980's. Some special features of the EES of the IVa and Va carbides were established[26,27], but the $(n+1)p$ states of the metal were excluded from the basis without justification. Other workers[28–31] calculated the EES of TiC, ZrC, NbC, and NbN by an empirical pseudopotential method. The CPW method was used[32,33] to construct the band structure of Ti and V oxides, and also NbN. Ichara[34] calculated the EES for the monocarbides of the TM in sub-groups IVa and Va and obtained a density of states distribution in excellent agreement with the X-ray photoelectron spectra of the carbides.

The most accurate calculations in terms of band models for a wide range of MX binary compounds (M = Sc, Ti, V, Nb; X = C, N, O) by a self-consistent CPW method with an X_α exchange potential were reported by Neckel and coworkers[35–45].

The $\varepsilon(k)$ dispersion curves (Fig.1) calculated for titanium carbide by the SCF CPW method[36] show a valence band structure characteristic of this type of compound: a low-energy sub-band composed mainly of $2s$ (C) states and separated from the $3d$(Ti) and $2p$(C) mixed states by a gap of ~3 eV, followed by a sub-band of $3d$, $4s$ states of the metal and by a free $3d$, $4s$ band. The Fermi level lies in the overlap region of the p,d and d,s bands, which accounts for the metallic properties of these compounds.

The changes in the relative contributions from different states to the valence band in the carbide, nitride, and oxide series are shown in Fig.2 by the energy distribution of the partial densities of states $g_i(\varepsilon)$ for the MX compounds (M = Ti; X = C, N, O)[36]:

$$g(\varepsilon) = g_s^X(\varepsilon) + g_p^X(\varepsilon) + g_d^M(\varepsilon) .$$

Several problems in the methodology of applying local (cluster) models to the electronic properties of refractory compounds are discussed in Refs.58 and 59. It is stressed that the main features of the EES spectrum and the changes in the valence band in the carbide, nitride, and oxide series are accurately reflected by cluster calculations. Furthermore, the results from band and from cluster methods for the same level of approximation (CPW and X_α-SW) and using the same input parameters are not only qualitatively similar but they lead to quantitatively similar distributions of electrons in space and energy[59]. This confirms the validity of descriptions of the EES of high-melting compounds based on local models. The distribution of total charge density in MX crystals leads to the same conclusion: it can be inferred from X_α-DV calculations fro the $CTi_6C_{12}Ti_8$ cluster in titanium carbide[132] and from calculations for NbC and NbN by the pseudo-potential method[30].

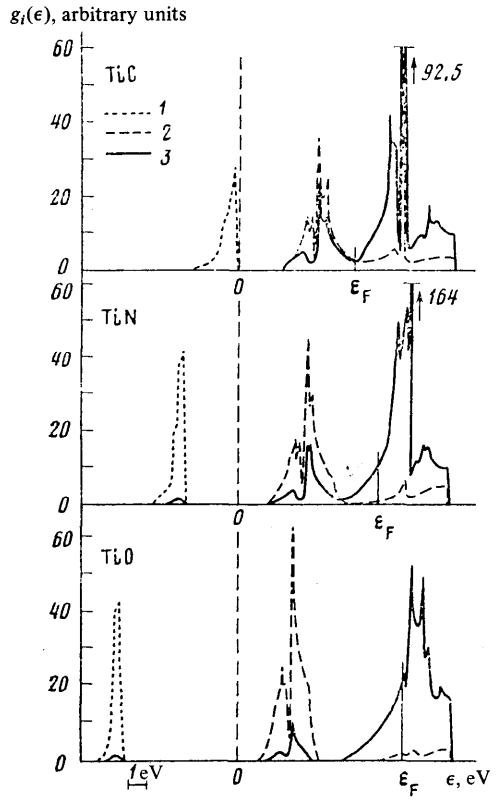


Figure 2. Partial densities of valency states[36] for TiX (X = C, N, O): *1*) and *2*) $2s$ and $2p$ states of X; *3*) $3d$ states of Ti.

The main features of the structure of the valence band and of the changes in this band for the series of binary compounds revealed by band[26–56] and by cluster calculations[57–71] can be summarised as follows.

1. The low-energy $2s$(X) band, which includes small contributions from the s, p, and d states of the metal, is broadened and shifted towards higher energies in the transition from oxides to carbides and from sub-group IVa to sub-group Va metals. For the carbides and nitrides of Hf and Ta (whose oxides with a B1 structure are unstable) the $4f$ states are found to be core states and practically unaffected by chemical bonding[55,56,63].

2. The band mainly responsible for valence bonding is formed by the strong mixing of the $2p$(X) and d(M) functions. It rapidly widens on going from oxides to carbides, and less rapidly on replacing the IVa by a Va sub-group metal. The overall covalency is higher in the Va than in the IVa metal compounds, and increases with the atomic weight of the metal within each sub-group.

3. The high-energy partially filled conduction band is mainly of the nd(M) type with a small contribution from $2p$(X), $(n+1)p$(M) and $(n+1)s$(M) functions, and it widens very rapidly on going from the oxide to the carbide. This is accompanied by a downards shift of ε_F and by a decrease in the density of states at the Fermi level $N(\varepsilon_F)$.

The redistribution of the individual atomic states during the formation of interstitial phases causes partial charge transfer between metal and non-metal atoms and contributes an ionic component to the chemical bond.

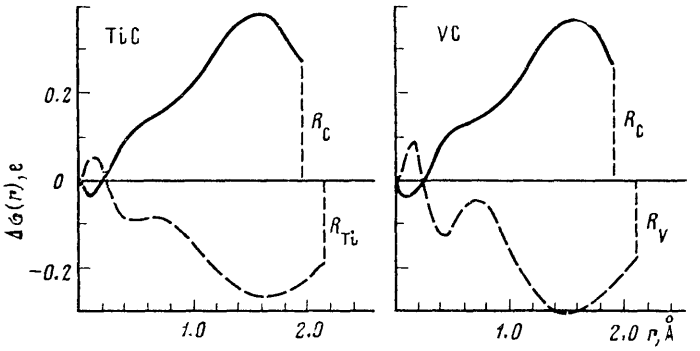


Figure 3. Difference between the crystal charge density (CPW) and the sum of the atomic charge densities in TiC and VC[36].

Strongly opposed views on the direction and magnitude of the charge transfer in MX compounds are held by different workers. Some[22,23] find that charge is transferred in the X → M direction. Others conclude from X-ray results[72,73] that the ionisation of the atoms in MX is very high (for example, almost +4 for Ti in TiC), and therefore they believe that the electrostatic energy is equivalent to ~90% of the cohesive energy of the crystal. However, the assertion[72,73] that the excess charges are strongly localised on the atoms is incompatible with most of the reported cluster and band calculations, with high-precision measurements by X-ray emission and photoelectron spectroscopy of the shifts in the internal levels for a wide range of carbides, nitrides, and oxides[36,37,53,54,57-70], and with the discussion in Section IV of this Review. Fig.3 shows the difference between the radial charge densities obtained in CPW calculations[36] for TiC and VC (σ_{cryst}) and as a superposition of the atomic densities (σ_{at}):

$$\Delta\sigma(r) = \sigma_{cryst}(r) - \sigma_{at}(r) .$$

In this case the excess of charge in the atomic spheres (i.e. the effective charge localisation on the atoms), given by

$$q^{eff} = Q_{cryst} - Q_{at} = \int_0^R \Delta\sigma(r)\,dr$$

is not large (~1e). There can be little doubt, at present, that charge transfer takes place in the M → X direction. The quantity q^{eff} increases slightly in the carbide, nitride, oxide sequence (see Table 2), thus increasing the coulombic contribution to the bond, but it remains much lower than the values postulated in the ionic model (+2, +3, and +4 for the metal in MO, MN, and Mc respectively).

By examining the atomic and the orbital composition of each type of state in the different energy ranges of the spectrum[35-37,57,59,63,64,69-71] it has been possible to identify the individual interatomic interactions and their relative contributions to the combined covalent-metallic-ionic bond found in high-melting phases. The crystal field causes splitting of the d(M) states, which become doubly (eg) or triply degenerate (t_{2g}). The t_{2g} states lying near ε_F are responsible for the M-M bond, and they are largely delocalised though they retain some thickening of the electron density in the M-M direction, characteristic of bonding interactions[62,63]. However, the system is diffuse and the M-M interaction is weak. The main chemical bonding effects are due to the strong interaction of the nd(M) and $2p$(X) functions, which forms interatomic bonds of σ and π type giving a three-dimensional network of orbitals with $eg(d_{x^2-y^2}, z^2)$ and $t_{2g}(d_{xy}, yz, xz)$ symmetry. As a result, the high-melting compounds are largely covalent, with a small ionic component in the bond.

Table 2. Orbital occupancies and charges (q^{eff}) on the metal atoms in the carbides, nitrides, and oxides of Ti, V, Zr, and Nb,[69-71]

Compound	$3d_\sigma$	$3d_\pi$	$3d$	q^{eff}	Compound	$4d_\sigma$	$4d_\pi$	$4d$	q^{eff}
TiC	0.85	0.44	2.97	0.50	ZrC	0.70	0.49	2.77	0.23
TiN	0.53	0.62	2.93	0.64	ZrN	0.42	0.71	2.89	0.42
TiO	0.31	0.79	3.02	0.78	«ZrO»	0.26	0.80	2.91	0.59
VC	0.97	0.70	4.05	0.39	NbC	0.78	0.79	3.95	0.24
VN	0.61	0.90	3.91	0.54	NbN	0.51	0.95	3.88	0.40
VO	0.35	1.05	3.96	0.67	NbO	0.34	1.14	4.10	0.54

The proportion of σ bonding is highest in titanium carbide, though the population of the π orbitals is double that of the σ orbitals. A marked redistribution of the occupancies of the t_{2g} and eg orbitals occurs in the carbide-nitride-oxide series, accompanied by a weakening of the σ bond (see Table 2). This results in destabilisation of the oxide lattice, making these compounds less refractory and less hard than the carbides[60,67,69-71].

These properties of the EES and of the charge distributions have been used to interpret X-ray emission[34,39,44,58-71] and photoelectron spectra[34,40,58-64,66,71] and appearance potential spectra[40], and also in studies of magnetic susceptibility[76], superconducting transition temperature[43], electronic specific heat[121,122], Hall coefficient[120], and Compton scatter profiles[74] for outlining the Fermi surface[34,75].

We should stress that all these calculations were for ideal, stoichiometric compounds, and in many cases (TiO, VO, VC, "ZrO") they were only model calculations.

IV. X-RAY EMISSION AND PHOTOELECTRON SPECTRA OF MX COMPOUNDS

Before attempting to describe the special features of the electronic spectrum of non-stoichiometric compounds we shall discuss the relationship between existing calculations for stoichiometric MX compounds and experimental data.

The experimental methods offering the most direct information on the distribution of electronic states over the whole depth of the valence band and on the energetics of the core levels are the spectroscopic X-ray photoelectron (XPS) and

X-ray emission spectroscopy (XE) methods. Spectral studies of most of the high-melting compounds discussed in this review have been reported (see Table 1). However, the extensive literature which has accumulated on this topic is literally "choked" with erroneous results: Zhurakovskii's recent monograph[126] is no exception. We shall not attempt to account fully for the inconsistencies in the experimental data, though the following general comments on the experimental problems of XE and XPS measurements on transition metal compounds may be helpful. On the one hand, errors in the calibration of the apparatus must lead to errors in the comparison of spectra from different series of components, and on the other hand errors can arise from differences in the surface layers of the samples electrically excited in the X-ray spectrometer.

Table 3. Bibliography of quantum-chemical calculations and X-ray emission and photoelectron spectroscopy work on non-stoichiometric compounds of the *d* metals.

MX_x	Band calculations		Cluster calculations		XE spectra	XPS spectra
	VC-CPW	CP	X_α	semi-empirical		
TiC_x	—	[124, 128]	[132]	[117, 129, 130, 136]	[129, 136, 137, 158]	[130, 138, 139, 147]
TiN_x	—	[125]	—	[129]	[142, 158]	[106]
TiO_x	[120]	[128]	—	[129, 131]	[85, 129, 131, 142, 143]	[99, 149]
VC_x	[34, 121, 122]	[127]	—	[129]	[85, 145]	[34, 147, 150]
VN_x	—	—	[134]	[129]	[144, 145]	[106]
VO_x	—	—	—	[129]	[85]	—
NbC_x	—	[127]	[133, 134]	[129, 135]	[87, 88, 146]	[98, 147, 148]
NbN_x	—	—	—	[129]	[145, 146]	[148, 159]
ZrC_x	[34]	—	—	[129]	—	[34]
HfC_x	—	[127]	—	[117]	—	—
TaC_x	[34]	—	—	—	—	[34]

The experimental results quoted in Tables 1–3 are those which we consider most relevant and useful to the present discussion. Interested readers wishing to examine the topic in more detail are referred to Zhurakovskii's monograph[126], which gives a full discussion of this type of work in the Soviet Union and abroad.

Measurements of the X-ray photoelectron spectra yield information on the density distribution of occupied electronic states over a wide range of energies[102] to the precision of the difference in photo-ionisation cross-section of the electronic sub-shells. The XPS spectra of the following compounds have been studied: TiC,[34,89,91–93] TiN,[92,94,95] VC,[34,90] ZrC,[34] NbC,[34,89,97] NbN,[97] NbO,[96] and HfC and TaC.[34] A series of XPS spectra for the valence band of *d* metal carbides has been obtained[34], and their parameters have been compared with CPW band calculations (Fig.4). Since the elements of the matrix which describes the transition probabilities in this energy region were assumed to be constant, the integral energy distribution of photoelectron intensity was compared directly with the calculated state densities. The relative intensity of peak II was found to increase in the TiC, ZrC, HfC series (Fig.4), and this was ascribed to the increase in the scattering cross-section of *d* electrons in the sequence 3*d*(Ti), 4*d*(Zr), 5*d*(Hf), since these electrons provide the main contribution to this part of the spectrum. Calculations based on the ionisation cross-sections of the sub-cells (after Scofield[103]) gave good agreement with experiment.

In the carbides of sub-group Va metals in the high-energy region we find a clear "outcrop" associated with the appearance of an additional *d* electron, and the relative intensity of peaks I and II increases with the atomic number of the metal (as in the carbides of sub-group IVa transition metals). Some of the difference between the theoretical and the experimental XPS spectrum of VC is due to the fact that stoichiometry was assumed in the calculation.

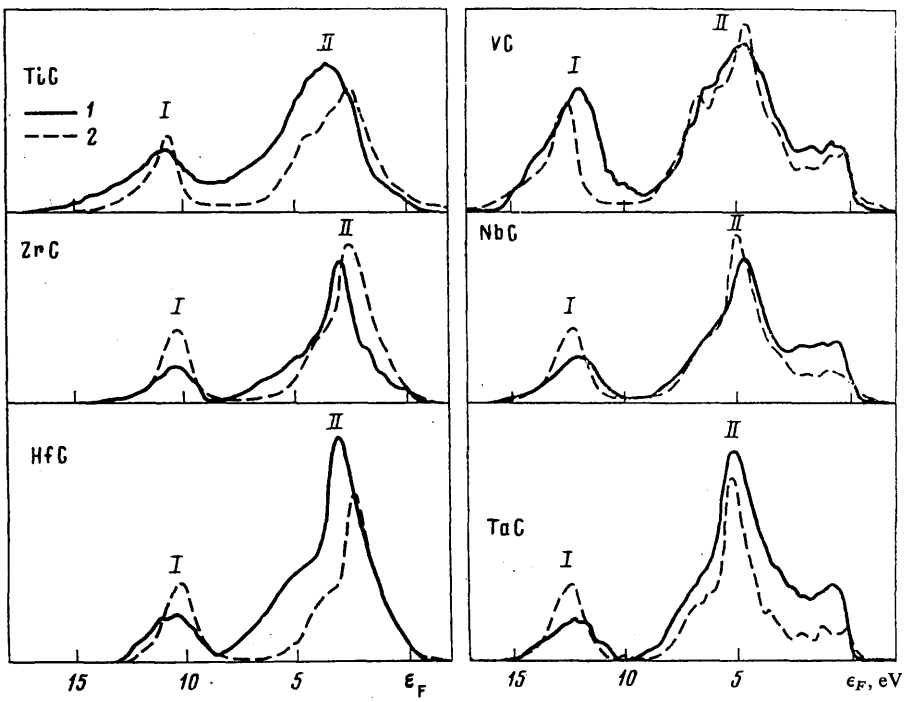


Figure 4. Experimental (*1*) and theoretical (*2*) XPS spectra of the carbides of transition metals in sub-groups IVa and Va.[34]

The relative advantages of band and cluster models for describing the XPS spectra have been discussed[58] in the case of TiC and VC. In the cluster approximation the spectrum was constructed by using the Gelius scheme[104], in which the intensities of the individual peaks (I_j) are defined in terms of the atomic photo-ionisation cross-sections σ_i:

$$I_j \sim \sum_i C_{ij}^2 \sigma_i ,$$

where C_{ij} are the coefficients of the MO in the LCAO expansion of the wave function. It was shown that the shape of the spectra for this class of compounds can be reproduced as accurately by the cluster approach as by band calculations if the bands are reasonably well localised.

As well as giving information on the structure of the valence band the XPS method can be used to measure the shifts in the core electron energy levels produced by the formation of mixed states in condensed phases, and it is an effective analytical technique for determining both the character of the chemical bond and the extent of charge transfer between the atoms[102].

Table 4 shows the changes in the energy ΔE of the inner levels of the carbides of the transition metals and the charges on the atoms (q^{eff}) calculated from data by Ramqvist[105] and Ichara[34]. We note that in all the carbides the shifts of the carbon levels are negative, and those of the metal levels are positive (relative to the energies of the corresponding levels in the neutral atoms). Thus a partial negative charge develops on the metalloid, and a partial positive charge on the metal. The discrepancy between the q^{eff} values obtained from data in Refs.34 and 105 is probably due to differences in surface preparation techniques in the two laboratories: in less carefully lapped surfaces[105] we expect a tendency for ΔE to increase.

Measurements[106] of the shifts of the 1*s*(N) and 2*p*(M) levels in the ScN, CrN, TiN, and VN series showed that in the nitrides also a small positive charge is localised on the metal atom, increasing from ScN to VN.

Table 4. Changes in the energies of core levels (ΔE, eV [105]) and in the ionic charges in TM carbides (q^{eff}). [34]

Carbide	$-\Delta E_C$	ΔE_M^*	q_M^{eff} (Ref.105)	$-q_C$	q_M	$\langle \lvert q_{C,M} \rvert \rangle^{**}$
TiC	3.3	1.3	0.40	0.25	0.13	0.19
ZrC	3.7	—	0.45	0.27	0.08	0.17
HfC	4.0	—	0.48	0.26	0.04	0.15
VC	2.6	1.8	0.32	0.15	0.17	0.16
NbC	2.9	1.2	0.35	0.17	0.24	0.20
TaC	2.9	1.6	0.35	0.16	0.27	0.22

*The ΔE_M values for $2p_{3/2}$(Ti), $2p_{3/2}$(V), $3d_{3/2}$(Nb), and $4f_{7/2}$(Ta) are given.

** Mean of the absolute values of q_C and q_M.

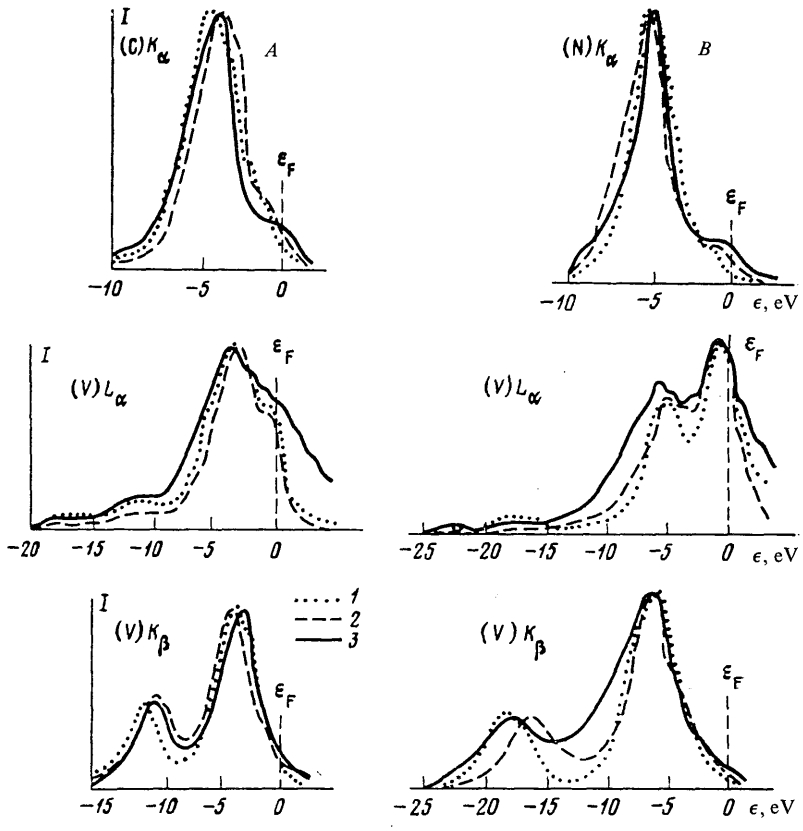


Figure 5. X-Ray emission spectra of VC (*A*) and VN (*B*): *1*) X_α-SW calculations, *2*) CPW calculations, *3*) experiment[59].

Direct calculations of the energy levels of the core electrons have been made by non-empirical X_α-SW and X_α-DV methods in a full basis for TiC, VO, and TiO.[107,108]. Allowance for relaxation effects (rearrangement of the electron shells under the influence of holes on the inner and valency levels) was made in Slater's transition state scheme[109]. Comparison of these results with the MO diagrams given by "unrelaxed" calculations shows that the valency states are almost unaffected, and that the uncorrected values can be used to calculate the energies of emission transitions. Relaxation effects become predominant for the inner levels, and by allowing for these effects we can calculate the absolute energies of the core levels in good agreement with XPS data.

More detailed information on the electronic energy spectra of high-melting compounds, including the configuration of the partial states of the individual components, can be obtained by the X-ray emission spectroscopy method[110]. Although the X-ray emission K, L, and M spectra of high-melting compounds have been observed by many workers (see Ref.10) their correct interpretation had to await the development of band calculations for TiC, TiN, and TiO,[24] and the identification of the long-wave satellites in the spectra of carbon, nitrogen, and oxygen compounds[81,111]. Even more exact interpretation of the XE spectra was made possible by cluster calculations[66,69,70].

In Fig.5 we show as an example the (C)$K\alpha$, (N)$K\alpha$, (V)L_{III}, and (V)$K\beta_5\beta''$ spectra of VC and VN [39] corresponding to the emitting transition $2p \rightarrow 1s$ (for C and N) and $3d, 4s \rightarrow 2p$ and $4p \rightarrow 1s$ (for V). By presenting these results on a unified energy scale with allowance for the different binding energies of the core electrons we find that a strong $2p$(X)–d(M) interaction occurs in all the compounds. The change from VC to VN affects most strongly the (V)L_{III} band: a high-energy element of structure is split off and produces a strong band, indicating an increased electron concentration in the nitride, with occupancy of the higher orbitals. In the (V)$K\beta_5\beta''$ spectrum of VN the $K\beta_5$ and $K\beta''$ sub-bands are significantly shifted towards longer waves, due to the decrease in the energy of the $2p$(N) and $2s$(N) states [as compared to the energy of the $2p$(C) and $2s$(C) states].

Correlations between the results of calculations by band methods and XE spectroscopy data are usually made in terms of the partial density of states $g(\varepsilon)$. The radial probabilities of emitting transitions have also been included in some calculations[39,44,112] of the intensities of XE spectra. The XE spectra calculated in this way for VC and VN by the X_α SW and CPW methods are shown in Fig.5. We note that (as in the XPS spectra) the main features of the XE spectra are satisfactorily described by small cluster calculations (both the position in energy of the maxima and their relative intensities), in full agreement with the results of CPW calculations[59].

The theoretical formulations[59–64,69–71] of the XE spectra of the carbides, nitrides, and oxides of Ti, V, Zr, Nb, Hf, and Ta allow a full interpretation of experimental data as well as the prediction of as yet unreported lines.

Thus the extensive applications of results from theoretical calculations and from spectroscopic investigations has yielded meaningful information on the EES and on the chemical interactions of high-melting compounds. As we shall show below, this approach has been successfully applied in studies of the rearrangement in space and energy of the electronic states caused by the appearance of structure defects.

V. ELECTRONIC STRUCTURE OF THE NON-STOICHIOMETRIC CARBIDES, NITRIDES, AND OXIDES OF THE *d* METALS

The marked effect of lattice vacancies on all the physicochemical properties of refractory compounds is well known[3–10]. Attempts to relate the observed dependences (of the property–defect density type) to changes in the electronic spectra led to the development of a number of qualitative models of the band structure in non-stoichiometric compounds, and stimulated some numerical calculations.

1. Phenomenological Models

The first attempt to allow for the effect of a variable concentration of vacancies on the EES of MX_x compounds relied on the rigid band model. It was assumed that the perturbation introduced by a vacancy into the crystal is generalised and does not affect the shape of the $N(\varepsilon)$ curve: only the occupancies are affected, depending on the concentration of valence electrons. By applying this postulate to calculations for stoichiometric TiC it was found[23] that an increase in the concentration of non-metal vacancies ($N_\square$) in the TiC_x compounds shifts the Fermi level towards the low-energy side of the spectrum, passing through a value (at the composition $TiC_{0.5}$) corrresponding to a maximum density of states in the bonding p–d band. We note that this conclusion is in sharp contrast with more recent XE [129,136,137,158] and XPS results [130,138,139], all of which imply a shift of ε_F in the opposite direction.

By using the same model Denker[113] explained the high equilibrium concentrations of vacancies in TiO_x in terms of the general decrease in the concentration of valence electrons (as compared to the stoichiometric composition), leading to a decrease in ε_F and in the total energy of the system and therefore to stabilisation of the structure. However, the neglect of the individual features of the band structure in particular compounds leads to the (generally incorrect) conclusion that any compound must be stabilised by the addition of vacancies.

Conversely, in the valence electron model[114] the defect is treated as a local perturbation of the electronic states in the crystal. When a non-metal atom is removed from an octahedral hole in the metallic matrix some of the previously screened M–M bonds become unscreened and can pass through the centre of the vacancy, and the d electrons set free by the breaking of the M–X bonds are accommodated in the high-energy local levels associated with the vacancy. As $N_\square$ increases, the local levels merge into a band: the result for the monocarbides of the IVa transition metals is a linear increase in ε_F, whereas for the monocarbides of metals in the Va sub-group a more complex dependence is obtained. Many changes in the kinetic and magnetic properties of monocarbides in their homogeneity region have been explained successfully by using this model[115].

Ichara's model[34], which is closely related to this theory[114], treats the EES of defect carbides as a superposition of the densities of states for the stoichiometric compound and for a hypothetic metal (with a face-centred cubic lattice) which forms clusters in the carbide structure by the conversion of carbon sites into carbon vacancies. The presence of strong M–M bonds in this case should lead to a stable value of ε_F.

Whereas the charge on the vacancy is not specified in the above models, Goodenough[116] proposed a model in which the vacancy carries a high charge (-2 for TiO_x) to compensate for the decrease in the Madelung energy in defect crystals, thus causing energy stabilisation of a substantial concentration of vacancies at equilibrium.

In the configurational electron localisation model[9] the main parameter used to define the electronic properties of the system is the statistical weight of an atom with stable configurations (SWASC), which is a measure of the deviation of the electronic configurations of the atoms in a stated compound

from the most stable configurations (i.e. free, half-filled, and completely filled). For the non-metal atoms in these compounds the stability of the bond is determined by the quasi-stable sp^3 configuration, whereas for the transition metals the maximum bond stabilisation corresponds to the d^5 configuration. The changes in the relative contributions of the various atomic states to the M–M and M–X bonds resulting from deviations from the stoichiometric composition are determined, according to this model, by the SWASC sp^3 and d^5. For example, for the compositions $TiC_{1.0}$ and $TiC_{0.67}$ semi-empirical estimates of these parameters give[117] 40.13 and 39.50% (SWASC sp^3) and 36 and 52% (SWASC d^5) respectively, indicating a weakening of the contribution from the p states to the strongest M–X bonds and a slight increase in strength of the M–M interactions in the defect carbides. These conclusions are qualitatively consistent with the development of metallic properties (increase in magnetic susceptibility, in low-temperature electronic specific heat, and in electrical conductivity) and with the decrease in micro-hardness and in T_f in carbides with a carbon deficit.

These phenomenological models of the electronic structure of non-stoichiometric phases offer a qualitative description of some of the experimentally observed variations in the physicochemical properties of MX compounds in their homogeneity region, but they cannot of course give any quantitative measure of the changes in the EES in space and energy: the parameters used in these models (such as the SWASC and the concentration of valence electrons) lend themselves only to the roughest qualitative estimates. Therefore the further development and quantification of our understanding of the nature of the chemical bond, of the interatomic interactions, and of the EES in these materials had to await the publication of correct quantumchemical calculations for individual compounds.

2. Calculations Using Band Models

Several calculations in which band methods are applied to non-stoichiometric compounds have been published (see Table 3). The first numerical calculation[119] by the strong bond method for TiC_x ($x = 1.0$, 0.8, 0.6) with explicit allowance for the presence of vacancies gave a Fermi level ε_F increasing with the concentration of defects in the non-metal sub-lattice. The next group of calculations for TiO_x,[120] VC_x, ZrC_x, and HfC_x,[34,121,122] relied on the virtual crystal approximation (*VC*-CPW), proposed by Schoen[123]. In this method allowance for the presence of vacancies was made by introducing functions of the concentration of vacancies into the expressions for the potential and for the matrix elements. The result was that the insertion of vacancies (whether in the metal or in the non-metal sub-lattice) does not produce new valency states which could be interpreted as vacancy levels[114] in any of the compounds examined. In a calculation[120] of the energy of formation of vacancies in TiO_x the difference between the bottom of the conduction band (which is fixed for all compositions) and ε_F was used as an average value of the energy for different compositions. This makes an oxide containing ~15% of vacancies in each sub-lattice the most stable composition[120]. It was also found[34] that as the concentration of X decreases, the energy of bands of the $2s$(X) and $2p$(X) type increases, but that of the d(M) type is relatively unaffected; the level ε_F decreases.

We should stress that these results were not confirmed by XPS measurements[34]: no significant shifts of the main spectral peaks were found, and an increase in the density of high-energy d states was noted. This inconsistency is due mainly to the use of ideal crystal potentials in the *VC*-CPW calculations for non-stoichiometric compounds[34,120–122], which is legitimate only for very low concentrations of vacancies.

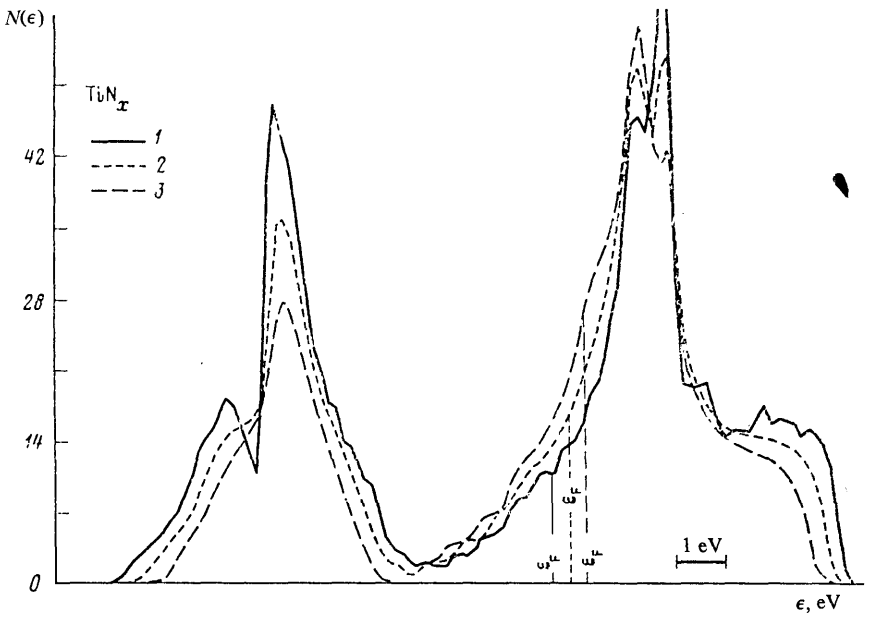


Figure 6. Full density of states in TiN_x; CP calculation[125] for $x = 0.0$ (*1*), 0.2 (*2*), and 0.4 (*3*).

This condition is not met in our case.

Calculations on TiC_x [124] and TiN_x [125] by the coherent potential (CP) method appear to be more reliable. In this work[124,125] the 2*s* states of C and N were excluded from the basis and assigned to the core states. An increase in $N_\square$ caused an increase in ε_F and a slight distortion of the energy dependence of the density of states (Fig.6). This is because an increase in $N_\square$ in TiC_x lowers the total number of carbon atoms in the *p* state, since $Np = 6-6_x$, whereas the number of expelled *p* electrons is $Npe = 2-2_x$. Under these conditions the Fermi level rises, and reaches the region of high density of states of the t_{2g} type. As a result $N(\varepsilon_F)$ also rises, as it does in the rigid band model, but for an entirely different reason, since in the rigid band model ε_F decreases, and the main contribution to $N(\varepsilon_F)$ comes from the e_g states.

Later calculations by the LCAO-CP method for NbC_x, TaC_x, and HfC_x ($0.7 \leq x \leq 1$) showed[127] that the spectra of sub-stoichiometric compounds do not contain any new structures identifiable as defect (vacancy) levels: the main effect is a small change in electron density $N(\varepsilon)$ as compared with the stoichiometric compounds, and the position in energy of the main $N(\varepsilon)$ spectral peaks stays almost constant, in contrast to earlier calculations[34,120-122]. In all the carbides ε_F moves upwards, the effect being most marked in HfC_x: $\Delta\varepsilon_F$ is 2.53 eV for $HfC_{0.7}$ as compared to 0.87 eV for $TaC_{0.7}$ and 0.72 eV for $NbC_{0.7}$. This is explained[127] in terms of the charge distributions in the carbides. In stoichiometric compositions a charge transfer of ~1*e* takes place in the M → C direction. Hence the removal of one C atom frees ~5 states, but only 4 electrons leave the crystal, so that 1 electron is transferred back to the metal and occupies its *d* band.

The parameters of the electronic structure of non-stoichiometric MX compounds calculated in this way[128] were used to calculate the energy of formation of defects in TiC and TiO. The formation of vacancies is due to the following common factors: 1) a change in the average energy of the bands, 2) the width of the band, 3) the creation of new levels of the defect type, 4) the position of the Fermi energy. A hypothetical binary compound AB was considered, with a band structure consisting of two bands (separated by an energy gap) corresponding to the states of the A and B components. It was shown[128] that the formation of vacancies in the sublattice of the atoms with lower electronic state energies can produce new (defect) levels with energies below ε_F, so that the total energy of the system is lowered by the transition of electrons to these new levels. This stabilising effect of the defect levels becomes more marked when ε_F rises as a result of an increase in $N_\square$. Under thse conditions the total

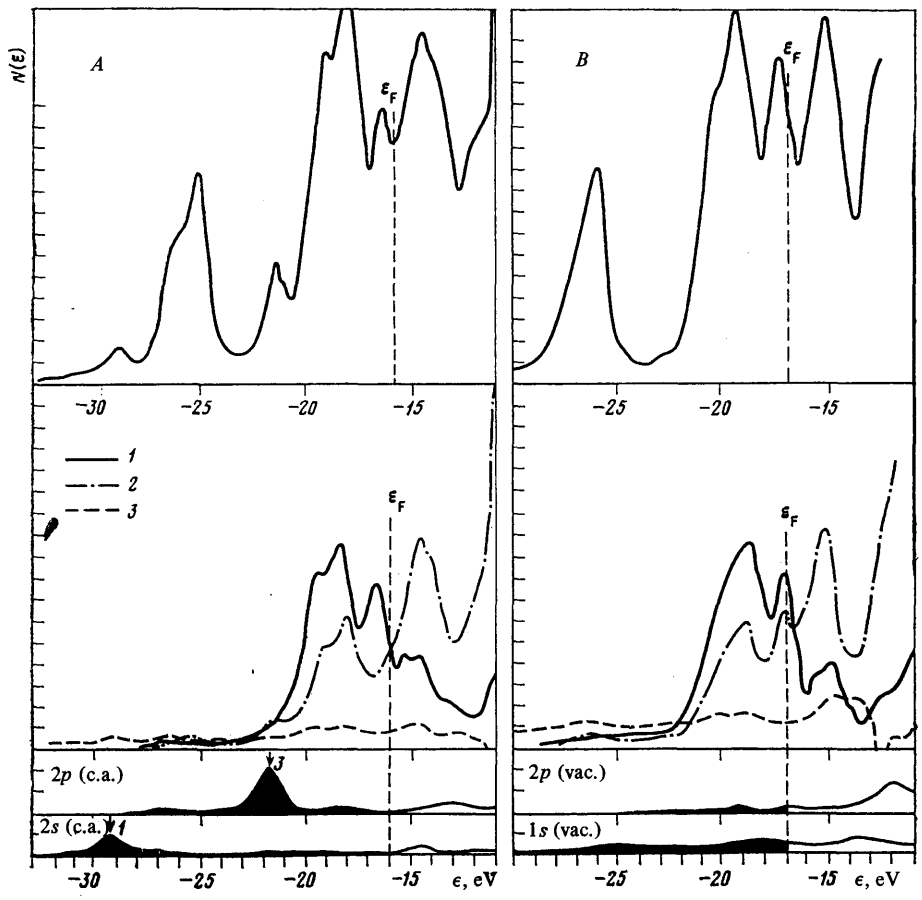


Figure 7. Full and partial densities of states in the stoichiometric cluster $CTi_6C_{12}Ti_8$ (*A*) and the defect cluster $\square Ti_6C_{12}Ti_8$ (*B*) used to model titanium carbide (X_α-DV method of calculation[132]): *1*) 2p(C), *2*) 3d(Ti), *3*) 4s + 4p(Ti). The lower outlines show the distribution of *s* and *p* states of the carbon central atom (c.a.) and of the vacancy (vac.).

energy of the system may go through a minimum at a certain concentration of vacancies, corresponding to the equilibrium concentration of defects. A calculation for TiC_x and TiO_x (by the Korringa–Kohn–Rostoker method in the averaged T matrix approximation) gave 0.0 ± 1.4 eV and 14 ± 1.4 eV respectively for the energies of formation of vacancies in TiC and TiO. Vacancy states lying below the Fermi level were found in the oxide but not in the carbide.

From the band calculations for MX_x compounds listed above[34,120–122,124,125,127,128] we may conclude that the general changes in band energetics and structure and in the position of the Fermi level are adequately described by this approach. However, problems concerning the rearrangement of the chemical bond in defect compounds and the nature of the vacancy states are largely unresolved. The solution of this type of problem, which basically arises from local changes in the electronic states close to a vacancy, was obtained by adopting cluster models.

3. Calculations by the Cluster Model

Several systematic calculations of the EES of carbides, nitrides, and lower oxides of the 3*d* and 4*d* metals (containing non-metal defects) by a semi-empirical SCF MO LCAO method in the cluster approximation have been reported[71, 129–131,136]. The vacancy was modelled by removing an X atom from the $[MX_6]$ fragment considered in the calculation (uncharged vacancy). As $N_\square$ was increased, the bands of $2s$(X) and $2p$(X) states became systematically narrower. The appearance of a vacancy is reflected most clearly by changes in the state of metal atoms in the immediate surroundings, since some of the *d* electrons genetically bound to these atoms are promoted to higher-energy levels, causing a sharp increase in the Fermi energy for compounds of metals in subgroup IVa. In compounds of the Va transition metals the shift of the Fermi level is much smaller.

The most important changes in the density of states take place near ε_F, because of the interaction[130,131] between nd and $(n+1)p$ orbitals of M in defect compounds. The occupancies also change, due to the increase in the charge of the cluster in the variable valency model. This model[129,136] assumes that the condition of overall electrical neutrality of the crystal can be applied to compounds of non-stoichiometric composition: $\sum_i x_i I_i = 0$, where x_i is degree of filling of the i-th sub-lattice, and I_i is the valency (state of charge) of its atoms. However, since (in TiC_x, for example) the carbon atoms keep the same surroundings, the valency of Ti should be lower in the non-stoichiometric than in the stoichiometric carbide in order to preserve the charge balance, and as a result the cluster containing vacancies acquires a partial negative charge. In this analysis the valency of the C atom is assumed constant, in keeping with the observed stability[139] of the $1s$(C) energy level in TiC_x.

This model was tested by comparing cluster calculations for sub-stoichiometric titanium carbides with the X-ray emission spectra[136]. Two variants of the calculation were described: for constant and for variable valency of the titanium respectively. In the latter case we observe the filling of the next higher metal *d* orbitals in the non-stoichiometric carbide, corresponding to the short-wave "outcrops" on the (Ti)L_α and (Ti)$K_{\beta 5 \beta''}$ bands of the emission spectrum of the $TiC_{0.65}$ sample. If constant valency of the Ti is assumed this effect is not found. The electronic energy spectra of NbC_x [133,134] and VN_x [134] compounds with non-metal defects have been studied by the X_α-SW method. The metalloid vacancy was modelled by an empty ("muffintin") sphere. The addition of a vacancy was found to raise the Fermi level by a small amount (~0.19 eV for NbC_x [133]). The changes in partial state densities arise from a slight redistribution of the states for the atoms adjacent to the vacancy and do not affect the more remote atoms, indicating a high level of localisation of the perturbations in the electronic distribution caused by individual vacancies. The rearrangement of the *d* states of the metal atoms nearest to the vacancies results in the appearance of a small charge in the sphere of the vacancy (0.7–0.8*e*), in contrast to the suggestion[116] that defects are highly charged. A new energy level, lying ~1.5 eV below ε_F, appears in the spectrum of occupied states.

The electronic nature of the vacancy in TiC_x has also been studied[132] by the non-empirical X_α-DV method. The calculation was carried out for a cluster of 27 atoms, using the pseudopotential from 96 external atoms as the boundary condition. Purely vacancy states were included in the basis in the form of 1s and 2p functions centred on the defect. These "vacancy" functions make a very small contribution to the filled band in the general spectrum of states (see Fig.7); since they are localised in the conduction band their perturbation is confined mainly to the spectrum of antibonding states. The change in structure of the states near the Fermi level following the introduction of a carbon vacancy has been ascribed[129–134] to the redistribution of the *d* states of the nearest metal atoms. Therefore the vacancy functions are localised (in space) within the first co-ordination sphere, and in energy well above ε_F (by 8–10 eV), and the presence of carbon vacancies does not produce any new occupied localised states.

As regards the charge on the vacancy, the additional electrons from the "broken" bonds are not captures by the vacancy (as shown by comparing the total charge density diagrams[132] for the integral and the defective cluster), and they fall into the 3*d* band of the metal instead. Similar conclusions are reached in calculations for clusters modelling vacancies in the metal sub-lattice[132]. Thus, since there is no marked localisation of the electrons on vacancies, the hypothesis of a continuously varying metal valency[129,130,136] in response to changes in the population of the 3*d* states caused by the formation of defects is confirmed.

We conclude that strict, non-empirical X_α-DV calculations have demonstrated the value of modelling the electronic structure of non-stoichiometric transition metal phases by extracting the appropriate atom from the fragment used in the calculation. They have also confirmed some earlier conclusions (see above) for other MX_x compounds which had been reached by semi-empirical MO LCAO methods[71,129–131,136].

VI. CALCULATION OF THE ELECTRONIC STRUCTURE OF NON-STOICHIOMETRIC COMPOUNDS FROM X-RAY EMISSION AND PHOTOELECTRON SPECTRA

For a long time the main problem in the study of non-stoichiometric MX_x compounds by XPS methods was the synthesis of sufficiently large single crystals (especially for studies of the valence bands). Therefore the early XPS measurements on non-stoichiometric compounds were limited to the effects produced by changes in the binding energy of the core levels [140,147]. XPS measurements of the valence bands became possible after the recent advances in the preparation of single crystals [which are so far limited to a few compounds, however (see Table 3)]. It was recently shown that almost metallic surfaces can be obtained by using hot-pressed samples of non-stoichiometric compounds[34,150], and that valence band studies by XPS are possible on these surfaces.

Let us examine the results of studies of MX_x compounds by XPS methods. Varying the composition of ZrC_x and TaC_x ($0.6 \leq x \leq 1.0$) did not produce substantial changes in the shape of the spectra[34]. Only some slight changes in the energy and width of peak II were noted (see Fig.8), together with a slight increase in the intensity of the "outcrop" on the short wavelength side of this peak, suggesting an increase in the occupancy of the t_{2g} band with decrease in the carbon content. We have already pointed out that this observation is inconsistent with the conclusions from VC-CPW calculations[34]. Conversely, by using the more strict CP method, changes in shape of the XPS peaks of NbC_x, HfC_x, and TaC_x consistent with experiment could be calculated[127]: in all these compounds an increase in $N_\square$ was found to produce a slight shift of the bands and a substantial increase in the sub-band close to ε_F (Fig.9).

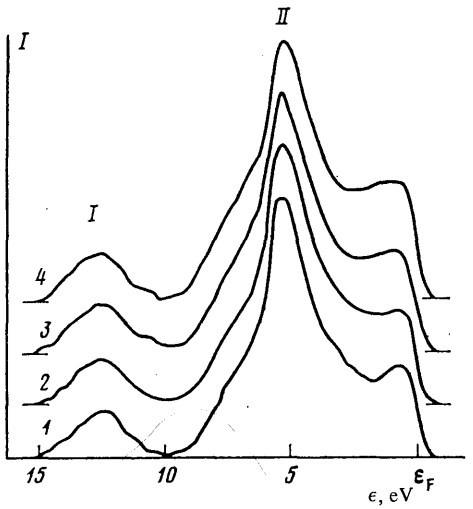


Figure 8. XPS peaks for the valence band of non-stoichiometric TaC_x [34] with the following x values: *1*) 1.0, *2*) 0.95, *3*) 0.9, *4*) 0.8.

A comparison[98] of the line shapes for $NbC_{0.98}$ and $NbC_{0.85}$ revealed a distinct new peak in the latter, located ~1.9 eV below ε_F, which was ascribed to the development of some p-type charge density localised in the sphere of the C vacancies[133].

The influence of variations in the number of defects on the XPS curve of TiC_x was studied by Johansson and coworkers[138,139]. They found that the half-width of the main peak, which reflects the range of p–d bonding, increases with $N_\square$. This effect was explained by MO (cluster) calculations[130] as an increased contribution from 3*d* electrons to the high-energy part of the filled band. Though this conclusion was confirmed by a special study[136] of the (Ti)L_α band in the X-ray emission spectra of carbon-deficient samples of TiC_x, the shape and the broadening of the reported XPS bands[138] need to be redetermined because the samples used in those measurements were contaminated with W which could have distorted the spectra because of its high 5d(W) electron photo-ionisation cross-section.

Table 5. Binding energy (ΔE) and chemical shifts (δ) of the core levels $3d_{5/2}$(Zr) and $4f_{7/2}$(Ta) in ZrC_x and TaC_x.[34]

ZrC_x			TaC_x		
1.0	179.3	0.4	1.0*	23.7	1.9
0.9	179.3	0.4	0.95	23.6	1.8
0.8	179.1	0.2	0.9	23.6	1.8
0.6	178.9	0.0	0.8	23.3	1.5
			0.7	23.3	1.5
			0.6	22.9	1.1

*For the 1s(C) level in TaC_x we have $\Delta E = 283.0$ eV and $\delta = -2.2$ eV; for the other levels 283.1 and −2.1 respectively. In the case of ZrC_x we have $\Delta E = 281.7$ eV and $\delta = -3.6$ eV for the 1s(C) state at all the values of x used in the work.

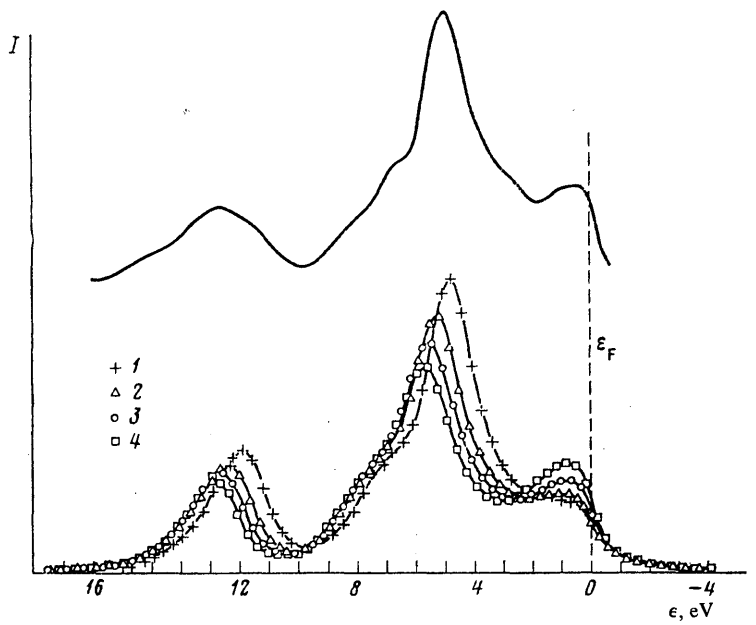


Figure 9. XPS spectra of TaC_x calculated[127] for x values of: *1*) 1.0, *2*) 0.9, *3*) 0.8, *4*) 0.7.

The photoelectron spectra of TiO_x [$x = 0.93$ or 1.15 (Ref.149), and $0.84 \leqslant x \leqslant 1.22$ (Ref.99)] showed a decrease in the intensity of the high-energy peak, which reflects mainly the 3d(Ti) states, with increasing oxygen content.

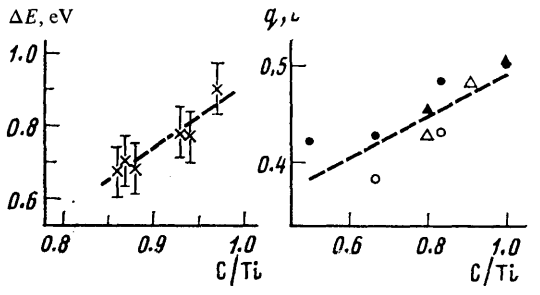


Figure 10. Shifts of ΔE for the $2p_{3/2}$(Ti) levels[139] and q^{eff} values for titanium[130] in TiC_x.

Interesting changes in the charge on the atoms in non-stoichiometric compounds were noted in measurements of the energy shifts of the inner levels of the X-ray photoelectron spectra of NbC_x,[148] NbN_x,[148] TiC_x,[138,139,147], and TaC_x and ZrC_x.[34] Shifts of the inner levels in low-carbon samples of TiC_x were also reported independently[140,147]. A systematic investigation of this effect[138,139] through the shift of the Ti $2p_{3/2}$ level showed a tendency for the shift to decrease as $N_\square$ increases (Fig.10), suggesting a change in the electronic configurations of the outer shells of Ti. Cluster calculations by the MO LCAO method[130] confirmed this. As Fig.10 shows, the effective charge q_{Ti} for clusters containing different numbers of vacancies decreases[130] as x decreases, denoting changes in the binding energy $E[2p_{3/2}(Ti)]$. Similar results have been reported[34] for ZrC_x and TaC_x (see Table 5). We note the fairly monotonic changes in the shifts $\Delta E[3d_{5/2}(Zr)]$ and $\Delta E[4f_{7/2}(Ta)]$, while the energy of the ls(C) levels remains practically constant: this can be ascribed to the constancy of the surroundings of the carbon atom in defect carbides, i.e. to the constant state of charge of the surroundings.

Attempts to examine the rearrangement of individual states in TiC_x as a function of N (by varying the energy of the exciting radiation) were inconclusive[139]. The use of X-ray emission spectroscopy methods seems more promising in this respect.

Most of the papers describing XE spectroscopic studies of the EES relate to non-stoichiometric oxides and carbides (see Table 3). For TiO_x ($x = 0.912$, 1.026, 1.19) the "centre of gravity" of the (O)$K\alpha$ band is shifted towards lower energies, and that of the (Ti)L_α band towards higher energies, by an increase in x, indicating[142] a decrease in charge density in the Ti and O spheres near ε_F and an increase in charge density in the deeper-lying states. Interesting rearrangements of the 4p(Ti) states have been observed[131] in a study of the (Ti)$K\beta_5\beta''$ spectra in TiO_x. In the region of non-stoichiometric compositions a high-energy structure element (K_{β_1}) was found, and its intensity was shown to increase with $N_\square$. The effect was interpreted[131] as a consequence of the 3d–4p mixing of the atomic orbitals of titanium on one lattice site, resulting from the lowering of the symmetry of the surroundings of the emitting atom produced by the formation of vacancies.

Direct confirmation of this conclusion was obtained in experiments with samples which had been exposed to high temperatures and pressures[131], in which the filling of vacancies (while retaining the overall composition $TiO_{0.88}$) caused a marked decrease in the intensity of the K_{β_1} sub-brand (see Fig.11). These results led to the recommendation[131] of X-ray emission as a method of calculating vacancy concentrations.

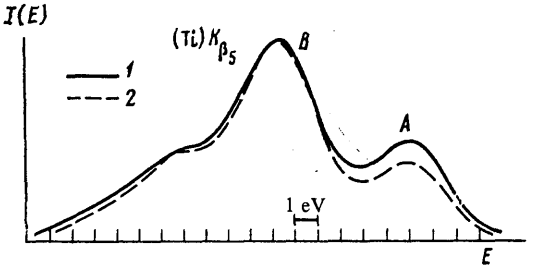


Figure 11. (Ti)K_{β_5} bands in the compound $TiO_{0.88}$: *1*) at normal pressure, *2*) at high pressure (90 kbar).[131]

The density of 3d(Ti) states near ε_F in titanium carbides is found to increase with $N_\square$ also from the behavour of the (Ti)L_α band[136,137], and direct confirmation of this increase has been obtained in cluster[129,136] and in band calculations[124]. A similar conclusion is reached from the shape of the (Nb)L spectra of NbC_x.[145] As regards the distribution of the 4p(Ti) states, identical Ti$K_{\beta_5}\beta''$ bands were observed for all the TiC_x compositions[126]. However, a more detailed study of $TiC_{1.0}$ and $TiC_{0.65}$ revealed[136] a clear $K^1\beta_5$ "outcrop" in the (Ti)K_{β_5} band of the non-stoichiometric compound which was absent in $TiC_{1.0}$ and can be interpreted as direct evidence of the appearance of 3d–4p interactions.

Far fewer studies of XE in non-stoichiometric nitrides have been reported. Nevertheless, existing X-ray emission L_α and $K_{\beta_5}\beta''$ spectra for compounds of composition TiN_x[142,158] and VN_x,[144,145] and calculations of the shape of the spectra by cluster (MO)[129] and band (CP) methods[125], suggest that the change in the valence band produced by an increase in the number of non-metal vacancies is the same for all the high-melting compounds of the transition metals: the density of d(M) states near the Fermi level increases, and the contribution from p(M) states (and also, in part, from the $2p$(X) electrons) also increases in this region. This conclusion is confirmed by the shape of the (X)K_α spectra of TiC_x, VC_x,[85,129,137], TiN_x, VN_x,[126,142,145] and TiO_x,[142,143] all of which develop a distinct "outcrop" on the short-wave side when $N_\square$ increases.

VII. THE CHEMICAL BOND IN NON-STOICHIOMETRIC MX_x COMPOUNDS

We shall now examine the changes in the chemical bond in non-stoichiometric compounds. As was pointed out above (Section III), in this class of compounds the bond is of a combined covalent–metallic–ionic type, and the existing descriptions differ in the relative contribution to the overall bond energy from the different types of interaction which they postulate.

Table 6. Populations (α) of the orbitals and of the interatomic bonds, and charges on the metal atoms, for some non-stoichiometric high-melting transition metal compounds[71,129].

Compound	$[MX_6]$ $(MX_{1.0})$					$[MX_6\square]$ $(MX_{0.856})$					$[MX_4\square_2]$ $(MX_{0.66})$				
	$(n+1)s$	$(n+1)p$	nd	q (M)	α (M – X)	$(n+1)s$	$(n+1)p$	nd	q (M)	α (M – X)	$(n+1)s$	$(n+1)p$	nd	q (M)	α (M – X)
ZrC_x	0.327	0.669	2.773	+0.235	0.619	0.360	0.675	2.792	+0.172	0.514; 0.616(2); 0.689(2)	0.405	0.602	2.894	+0.139	0.563 (2); 0.701 (2)
NbC_x	0.315	0.780	3.747	+0.158	0.558	0.327	0.662	3.884	+0.127	0.503; 0.662(2); 0.729(2)	0.359	0.585	3.966	+0.092	0.867(2); 0.649(2)
TiN_x	0.224	0.202	2.931	+0.642	0.330	0.221	0.195	2.982	+0.602	0.328; 0.411(2); 0.431(2)	0.212	0.176	3.050	+0.562	0.421(2); 0.447(2)
NbN_x	0.277	0.433	3.882	+0.408	0.411	0.283	0.329	4.012	+0.376	0.316; 0.383(2); 0.445(2)	0.349	0.367	3.871	+0.413	0.521(2); 0.599(2)
VO_x	0.154	0.219	3.968	+0.660	0.208	0.318	0.163	4.075	+0.630	0.197; 0.233(2); 0.256(2)	0.123	0.140	4.153	+0.585	0.239(2); 0.294(2)

Band calculations[119–122,124,125,127,128] suggest a number of conclusions on the change in relative contributions brought about by an increase in the number of defects. Thus an increase in the width and in the population of the metal d band[124,125,127,128] can be treated as a strengthening of the M–M interactions, whereas a narrowing of the $2p$(X) band is equivalent to a weakening of the interaction of the $2p$(X) and d(M) functions (the covalent component of the M–X bond).

A simple "energy diagram" of this type of redistribution can be produced[124] by noting that the breaking of M–C bonds produces an upward shift in energy of the d states of ~2.7 eV (in TiC_x), due to the $e_g \rightarrow t_{2g}$ ($d_\gamma \rightarrow d_\varepsilon$) transition. This increase in the occupancy ratio $N^M(t_{2g})/(N^M(e_g)$ (i.e. the strengthening of the M–M bond) caused by an increase in $N_\square$ has been ascribed[127] to charge transfer effects, arising from the reversion to the d_γ(M) band of the additional electron on the carbon atom when the latter is removed from the carbide lattice.

By far the most successful approaches in studies of the chemical bond are the cluster (MO) calculations, which offer a clear description of the origin and structure of the interactions between particles and allow the contributions from the different types of bond to be assessed quantitatively. The parameters of the electronic structure obtained from cluster MO calculations for a series of Ti, V, Zr, and Nb carbides, nitrides, and oxides[129] are listed in Table 6. We note that in both the stoichiometric and the non-stoichiometric compounds the main contribution to the chemical bond comes from the interaction between the nd functions of the metals and the $2p$ states of the ligands. As $N_\square$ increases, the occupancies of the individual M–X bonds also increase, but the total number of electrons involved in bond formation between the metal and the nearest ligands (expressed per metal atom) decreases from 2.45 for $TiC_{1.0}$ to 1.61 for $TiC_{0.5}$. Furthermore the addition of defects makes the electron density of individual bonds strongly anisotropic.

An increase in defect density rapidly lowers the charge (q^{eff}) localised on the atoms, thus making the role of the ionic component of the chemical bond even less important[117,129,130,132,136].

The changes in bond type brought about by a nearby vacancy are made clear by comparing the wave function diagrams for the σ and π types of interaction in stoichiometric and in non-stoichiometric titanium carbide[132]: this shows that the formation of a vacancy does not produce new bonds passing through the centre of the vacancy. The interactions between the states of the nearest metal atoms and those of the vacancy are quite complex, and they can be interpreted as a form of vacancy–metal π bonding. However, as the diagrams for the M–M interactions show[132], these bonds are the same as in the ideal carbide, and strong unscreened M–M bonds directed through the centre of the vacancy[114] are not formed.

Similar conclusions follow from cluster calculations modelling vacancies of metal atoms[132]: no electrons are localised on the vacancy, and no bonding states are created near the vacancy. Obviously, this explains the reported instability of metal vacancies in titanium carbide.

The changes in chemical bonding discussed above for the case of TiC_x apply also to other defect compounds of the MX_x type[129–131,135] (see Table 6).

In the carbide–nitride–oxide series the population of orbitals of the t_{2g} type increases (i.e. the M–M interaction increases), but the M–X bonds remain predominant over the whole of the homogeneity region (though their anisotropy increases). The total number of electrons localised on the M–X bonds decreases.

In the compounds of 4d metals (Zr, Nb), as in the stoichiometric compounds, the d(M)–$2p$(X) bond becomes stronger.

In the carbides of the sub-group Va transition metals various parameters (micro-hardness, thermal expansion coefficient, etc.) were found to have an extremum near the composition $MX_{0.8}$.[9,10,115].

These effects are probably related to the observed ordering of the vacancies[151–154] in MX_x. Evidently, more accurate descriptions can be expected from future calculations with clusters large enough to allow for ordering of the vacancies in the crystal structure.

VIII. THE ELECTRONIC STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF NON-STOICHIOMETRIC COMPOUNDS

Many studies of the physicochemical properties of high-melting compounds containing defects have been reported[3–10,115]. The results are usually interpreted in terms of simple qualitative models, and attempts to relate the observed changes to the parameters of the electronic structure, or indeed to calculate these parameters, are uncommon[127,129–136]. The only exception is the series of calculations (mentioned above) on XPS and XE spectra. This is due partly to the difficulty and complexity of strict quantum-chemical calculations of the electronic spectrum of defect phases, and partly to the difficulty of preparing samples with different vacancy concentrations while excluding microstructure effects (grains, domains, etc.) and chemical impurities, so that the observed differences in properties can be reliably ascribed to the different defect concentrations[3–10].

Nevertheless various correlations (of the electronic structure–property type) have been proposed[127,129–136,155,156]. To discuss these results we must examine first of all the method

used to calculate the EES of the compound. Depending on the specific features of the chemical bond and of the electronic structure, all the physicochemical properties which describe a high-melting phase can be classified into two groups[9]. The first includes the "lattice" properties such as micro-hardness (H_μ), T_f, atomisation energy, thermal expansion coefficient, etc. In the second group we classify all the magnetic and electrical properties determined by the distribution and concentration of high-energy delocalised *d* electrons. In this case calculations based on cluster (local) models are the most effective for describing the first group of properties, whereas approaches based on the band model are preferable for processes determined by the behaviour of almost fully collectivised electrons in a periodic crystal field.

Unfortunately, only a few qualitative comparisons have been possible so far, because of the very limited range of band calculations now available[127]: known anomalies in the phonon spectra of NbC_x and TaC_x can be explained by the redistribution of density of t_{2g} sub-bands, and the changes in $N(\varepsilon)$ can be shown to be qualitatively consistent with changes in T_S, ρ, the Hall coefficient, and the electronic specific heat.

More precise correlations have been possible by using the results of cluster calculations[129-136]. Changes in the "lattice" properties (decrease in T_f, H_μ, and atomisation energy accompanied by an increase in the amplitude of thermal vibrations $\sqrt{u^2}$ and in thermal expansion coefficient[157]) caused by an increase in $N_\square$ (Fig.12) are ascribed to the general weakening of the covalent M-X interaction resulting from the decrease in the total number of electrons localised on neighbouring M-X bonds and from the large increase in the anisotropy of individual bonds (see Table 6). The observed increase in magnetic susceptibility, and decrease in ρ, are consistent with the increase in the number of *d*-type electrons close to ε_F. In some calculations[129,131,132] the defects were assumed to be fully disordered. Long-range order[152-154] (with a type of ordering dependent of composition) should cause departures from monotonic dependences, as has in fact been observed for some of the parameters of the carbides of sub-group Va metals (see Fig.12).

The main weakness of the parameter (the overlap population) used by several workers[129-136] to explain the physicochemical properties of MX_x compounds is that it cannot be measured by direct experiment. An energy scheme developed[67] for calculating chemical bond stabilities in stoichiometric TiC, TiN, VC, and VN has confirmed earlier conclusions based on bond populations on the changes in bond energetics in this series of compounds. We can therefore expect these conclusions to be extended to energy effects in the bonds of non-stoichiometric compounds.

An interesting new application of EES calculations in the cluster model is in the interpretation of the NMR spectra of MX_x.[156] The observed parameters of the NMR spectra have been correlated with changes in overlap populations of different types (σ and π). Direct quantum-chemical calculations of the electric field gradient in VC_x, VN_x, and VO_x showed that at the nuclei this parameter is determined by valency contribution from the 3*d*(V) electrons. The calculated quadrupole interaction constants were in reasonably good agreement with experiment ($\nu_Q = 0.48$ and 0.164 MHz respectively for VO_x).

A calculation[134] by a non-empirical X_α-SW method gave a temperature (T_S) for the transition to the superconducting state in NbC_x and VN_x in qualitative agreement with the experimental value. These results justify the hope of substantial new progress in the application of cluster methods

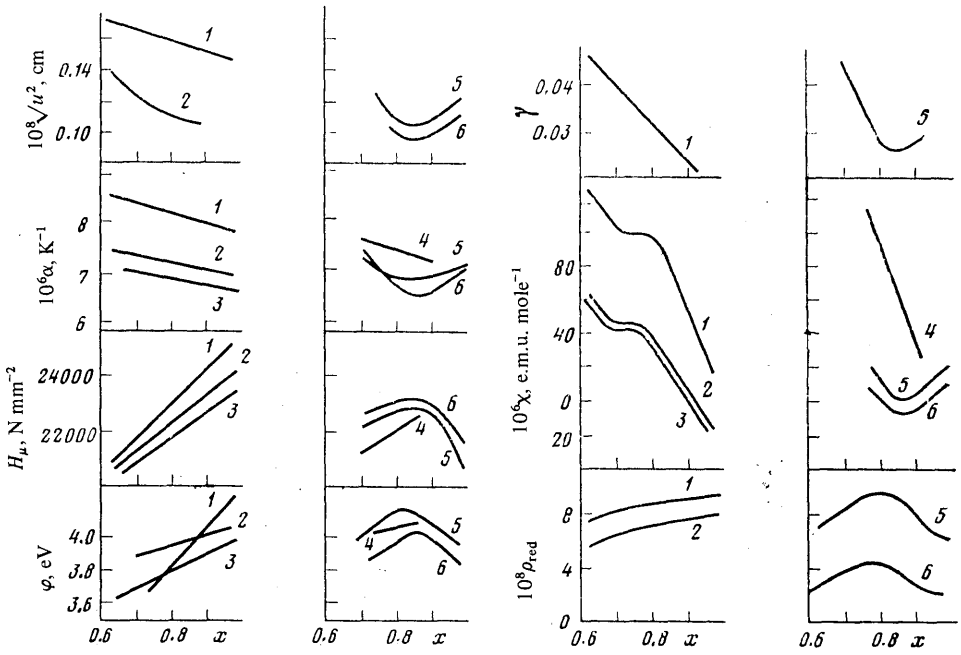


Figure 12. Changes in the amplitude of the thermal vibrations of the atoms ($\sqrt{u^2}$), thermal expansion coefficient (α), micro-hardness (H_μ), work function (ϕ), recombination coefficient of hydrogen atoms (γ), magnetic susceptibility (χ), and reduced electrical resistivity (ρ_{red}) in the homogeneity region of the carbides of: *1*) Ti, *2*) Zr, *3*) Hf, *4*) V, *5*) Nb, *6*) Ta.[9]

to the calculation of the physicochemical characteristics of defect phases.

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Thus the basic models and methods of calculation developed so far are adequate for meaningful studies of the EES of defect phases over a wide range of vacancy concentrations. The main features of the rearrangements in the electronic structure and of inter-particle interactions in MX_x compounds have been established. Further developments in our understanding of the EES of defect phases should include defect ordering and double defect structures. Another important future goal is the assessment of the energy of rearrangements in the chemical bond caused by the creation of vacancies, which could be immediately translated into a description of the mechanism of structural phase changes in MX_x. By developing a new formalism, and by adding to the existing fund of calculations of independently measurable physicochemical properties in the homogeneity region, new impetus could be given to the development of theoretical models of defect states offering a prescribed set of properties.

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Relation between the Nature of the Components of Titanium-containing Ziegler Systems and Their Activity and Stereospecificity in the Polymerisation of Dienes

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Problems concerning the influence of ionic-coordination catalytic systems and of the structure of their individual components on their stereospecificity and activity in the polymerisation of dienes are considered in relation to titanium-containing catalysts. Modern ideas about the structure of the active centres and the factors determining their stereoregulating capacity are also examined.
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I. INTRODUCTION

The development of studies on catalytic processes using systems of the Ziegler–Natta type opens up new possibilities for the separation of stereoregular polymers both by employing hitherto uninvestigated monomers and by varying widely the composition and conditions in the formation of the catalyst. The literature on this question is enormous particularly when patents are included. The titanium-containing catalytic systems, which have been most thoroughly investigated and have been most widely used, are convenient systems for examining the influence of the composition of the catalyst on the stereospecificity of the systems and their activity as well as certain kinetic characteristics of the polymerisation of dienes, primarily butadiene and isoprene. These data made it necessary to resort to modern ideas about the structure of the active centres and the factors determining their stereoregulating capacity.

II. THE INFLUENCE OF THE STRUCTURE OF THE COMPONENTS OF TITANIUM CATALYTIC SYSTEMS ON THE CHARACTERISTICS OF THE POLYMERISATION OF DIENES

It is known that, depending on the nature of the transition metal, the polymerisation of dienes in the presence of metal complex catalysts results in the formation of polymers with different stereoregularities. For example, the $TiCl_4$–AlR_3 system (Al : Ti ≅ 1) yields preferentially 1,4-*cis*-polyisoprene[1], while 1,4-*trans*-polyisoprene is formed in the presence of VCl_4–AlR_3.[2]

Catalytic systems based on the same transition metal are also capable of manifesting different stereospecificities. This is primarily because the metal in the active centres of the growing chains ($P-MX_n$) can exist in various valence states and can contain particular groups X at their reaction centre. The state of the active centre also changes when the polymorphic modification of the transition metal compound is varied. Allowance for these factors opens up wide possibilities for the regulation of the stereospecificity of catalytic systems[3] by altering the nature of the transition metal, its valence, and the structure of the ligand X. Thus it has been shown in relation to chromium-containing catalysts[4] that the variation of the ligands makes it possible to realise all the conceivable microstructures of polybutadiene and polyisoprene.

Table 1. The microstructure of polybutadiene obtained in the presence of various titanium-containing catalytic systems.

Catalytic system	Content of units, %			Refs.
	1,4-*cis*	1,4-*trans*	1,2-	
$TiCl_4$–I_2–AlR_2H–AlR_3	95.6	1.2	3.2	[5]
TiI_4–AlR_3	93–95	2–4	2–5	[6–8]
$TiCl_4$–AlI_3–$AlHCl_2 \cdot OR_2$	95	—	—	[9]
$TiCl_3 \cdot L^*$–AlR_2I	94	2	4	[10]
$TiCl_4$–AlR_2I–AlR_3	92.7	—	—	[11]
$TiCl_4$–I_2AlR_3	92	4	4	[12]
TiI_2Cl_2–AlR_3	92	4	4	[3]
Polytitanate-I_2-AlR_3	90	—	—	[13]
$TiBr_4$–AlR_3	85	10	5	[6]
$TiCl_2(CNS)_2$–AlR_3	78	10	12	[14]
$Ti(acac)_3$**–AlI_3–AlR_3	72	23	5	[15]
$Ti(acac)_3$–$AlBr_3$–AlR_3	64	24	12	[15]
$Ti(OR')_4$+$AlRCl_2$(Al : Ti=5)	63.5	34.5	2	[16]
$TiCl_4$–AlR_3(Al : Ti≅1)	55–60	36–41	4	[6, 7, 17, 18]
$TiCl_2(acac)_2$–AlR_3	59	16	25	[14]
$Ti(acac)_3$–$AlCl_3$–AlR_3	53	34	13	[15]
$Ti(acac)_3$–AlR_2Cl	50	38	12	[19]
$TiCl_2(OCOR')_2$–AlR_3(R'>1)	53	15	32	[14]
TiF_4–AlR_3	35	—	—	[20]
$TiCl_2$–AlR_2Cl	32	64	4	[21]
$TiCl_2$–AlR_3	0	94.5	5.5	[21, 22]
$Ti(OR')_4$–$AlRCl_2$(Al : Ti=10)	4	94	2	[16]
$TiCl_4$–AlR_3(Al : Ti≥2)	0	98	2	[18]
$TiCl_3(\alpha, \gamma, \delta)$–$AlR_3$	—	****	—	[23]
$Ti(NR_2')_4$–$AlRCl_2$	—	****	—	[24]
$TiCl_2(OR')_2$–AlR_3	21	31	48	[14]
$TiCl_2(Ind)$***–AlR_3	22	18	60	[14]
$Ti(OR')_4$–AlR_3	2–12	0	88–98	[25]
$Ti(NR_2')_4$–AlH_2NR_2	—	—	89–93	[24]
$Ti(NR_2')_4$–AlR_3	—	—	****	[24]

*L = 2-methyltetrahydrofuran.
**acac = acetylacetone.
***Ind = indenyl.
****The polymer chain consists predominantly of units of the given type.

Such universality is characteristic also of titanium-containing catalytic systems. Titanium systems of the Ziegler type make it possible to obtain highly stereoregular polybutadienes with all possible microstructures (Table 1) and a similar picture is also observed when organometallic titanium compounds are used (Table 2). There are as a rule no 1,2-units in polyisoprene obtained in the presence of titanium systems of the Ziegler type (Table 3). Up to 6–7% of 1,2-units is formed only with benzyl derivatives (Table 4).

Table 2. The microstructure of polybutadiene obtained from titanium-containing compounds with a titanium–carbon bond (R = benzyl; solvent—toluene).

Catalytic system	Content of units, %			Refs.
	1,4-*cis*	1,4-*trans*	1,2-	
R_3TiI	97	1	2	[37—41]
$R_2TiI—AlR_3'$	96	2	2	[41]
$R_3Ti—AlR_2'I$	93	4	3	[41]
R_3TiI	91	7	2	[41]
$RTiI_2—AlR_3'$	90	7	3	[41]
R_3TiI*	81	15	4	[40]
RTiI	68	29	3	[41]
R_3TiBr	66	13	21	[40]
$(CH_3)_3SiCH_2TiCl_3—C_2H_5Li$	64	32	4	[42]
$(ClC_6H_4—CH_2)_4Ti$	60.4	22.2	17.4	[43]
R_2TiCl	54	8	38	[41]
R_3TiCl	35	19	46	[40]
$RTiI_2$	32	55	13	[41]
R_4Ti	26	15	59	[37, 38, 40]
R_3Ti	25	13	62	[44]
tris-π-Pentenyltitanium	—	—	60	[45]
$[(CH_3)_3SiCH_2]_3Ti$	15	18	67	[42]
$[C_3H_5(CH_3)_2SiCH_2]_3Ti$	0	17	83	[42]
$[(CH_3)_3SiCH_2]_4Ti—C_2H_5Li$	0	8	92	[42]
$(CH_3)_3SiCH_2TiCl_3$	—	88.8	—	[46]
$RTiCl_2$	0	90	10	[41]
$R_4Ti—AlCl_3$ (1 : 4)	0	100	0	[43]

*Solvent—hexane.

Table 3. The microstructure of polyisoprene obtained in the presence of various titanium-containing catalytic systems (R,R' = alkyl groups).

Catalytic system	Content of units, %			Refs.
	1,4-*cis*	1,4-*trans*	3,4-	
$TiCl_4—AlR_3$ (Al : Ti≃1)	95—99.5	—	—	[1, 6, 26, 27]
$TiCl_2(acac)_2—AlR_2Cl$	97.5	1.4	1.1	[28]
$Ti(OR')_4—Br_2—AlR_3$	97.1	0	2.9	[29]
$Ti(OR')_4—AlBr_3—AlR_3$	96—97	—	—	[30, 31]
$Ti(OR')_4—AlBr_3—AlR_2Cl$	97	0	3	[32]
$Ti(OR')_4—R_3Al_2Cl_3$	96.5	0	3.2	[33]
$Ti(OR')_4—AlRCl_2$ (Al : Ti=4)	96	0	4	[16, 34]
$TiI_4—AlR_3$	*	—	—	[6]
β-$TiCl_3—AlR_3$	85	0	15	[23]
β-$TiCl_3—AlR_2Cl$	85	0	15	[23]
$Ti(OR')_4—AlRCl_2$ (Al : Ti=10)	58	38	3	[16]
$TiCl_2—AlR_3$	0	88	12	[21]
$TiCl_3$(α, γ, δ)$—AlR_3$	0	91	9	[23, 35]
$Ti(O-t-R')_4-AlRCl_2$	—	*	—	[34]
$TiCl_4—AlR_3$ (Al : Ti=2)	—	*	—	[36]
$Ti(OR')_4—AlR_3$	—	—	93—99	[25]

*The polymer chain consists predominantly of units of the given type.

Table 4. The microstructure of polyisoprene obtained in the presence of titanium-containing compounds with a titanium–carbon bond (R = benzyl, solvent—toluene).

Catalytic system	Content of units, %				Refs.
	1,4-*cis*	1,4-*trans*	3,4-	1,2-	
Tris-π-pentenyltitanium-Al_2O_3	91	0	9	0	[45]
R_3TiI	87	0	13	0	[47]
R_3TiBr	69	0	27	4	[47]
$R_4Ti—Al_2O_3$	60	0	—	—	[48]
Tris-π-pentenyltitanium	24	43	30	3	[45]
R_3TiCl	19	36	39	6	[47]
R_4Ti	0	75	18	7	[47]
R_2TiBr_2	0	94	6	0	[47]

With the exception of piperylene (Table 5), studies on the polymerisation of two conjugated dienes have not been systematic and have not embraced a wide range of catalytic systems. It is therefore difficult to infer the stereoregulating selectivity of titanium systems in relation to these monomers.

Table 5. The microstructure of polypiperylene obtained in the presence of various titanium-containing catalytic systems.

Catalytic system	Content of units, %			Refs.
	cis-	*trans*-	3,4-	
$Ti(OR')_4—AlR_3$	80—85	9—15	3—5	[49—50]
$Ti(OC_{10}H_{19})_4—AlR_3$	73	17	10	[51, 52]
$TiBz_4—AlBz_3—C_{10}H_{19}OH$	66	23	11	[52]
$TiCl_4—AlR_3$	61	36	3	[53]
$TiBz_4—AlR_3$	57	42	1	[54, 55]
$TiBz_4—C_{10}H_{19}OH$	53	35	12	[52]
$CpTiCl_3—AlR_2Cl$	36	63	1	[56]
$TiI_4—AlR_3$	6	92	1	[57]

Notation: R' = alkyl; $C_{10}H_{19}OH$ = methanol; Bz = benzyl; Cp = cyclopentadienyl.

1. The Influence of the Ligand Environment at the Titanium Atom on the Stereospecificity and Activity of the Catalyst

There are at present no experimental data characterising the structure of the active centres of Ziegler catalysts but the specific features of the active centres can be inferred at least comparatively from the microstructures of the polydiene.

Table 1 shows that in the polymerisation of butadiene the titanium-containing system exhibits a high *cis*-regulating capacity only if it incorporates iodine and, for the optimum component ratio, the form in which this element is incorporated in the system is not very significant: in the initial titanium compound (TiI_4, TiI_2Cl_2), in the elemental form (I_2), or as part of the composition of other components (AlI_3, AlR_2I). The benzyl derivatives of titanium provide a remarkable example of the fact that the presence of iodine at the titanium atom in the active centre does not alone ensure a high *cis*-regulating capacity of the catalyst in the polymerisation of butadiene. Thus a sharp difference between the stereospecificities of R'_2TiI (91% of 1,4-*cis*-units) and $R'TiI_2$ (32% of 1,4-*cis*-units) has been observed[41]. It is extremely instructive that, when the $R'TiI_2—AlR_3$ system is judged on the basis of the microstructure of polybutadiene (Table 2), its active centres are apparently identical with those of the R'_2TiI catalyst.

The data on the microstructure of polybutadiene justify the hypothesis that, in all cases where iodine-containing Ziegler systems are used (Table 1), identical active centres are formed with iodine in the coordination sphere of the titanium atom. This is also confirmed by the results of the study of substances formed in the $TiI_4—AlR_3$ and $TiCl_4—I_2—AlR_3$ systems[58]. It has been observed that reduction and halogen exchange reactions take place in the ternary system and that the deposit contains organotitanium(III) iodide. When titanium tetrachloride is reduced by diethylaluminium bromide, the amount of bromine which is added to titanium is also appreciably greater than might have been expected on the basis of the statistical redistribution of the halogens[59]. The ease of replacement of chlorine at titanium by bromine or iodine has also been observed when $TiCl_3$ is treated with certain bromine- and iodine-containing compounds (AlI_3,

$AlRI_2$, AlR_2I, $AlBr_3$, $AlRBr_2$, and AlR_2Br), which is accompanied by a change in the stereospecificity of the action of the $TiCl_3$–AlR_2Cl system[60]. It has been suggested[61] that the ease of halogen exchange between $TiCl_4$ and AlR_2I is due to the fact that the larger titanium ion combines preferentially with the more polarisable (larger in size) iodide ion, while aluminium combines preferentially with the smaller halide ion (the chloride ion).

Judging from the microstructure of polydienes (Tables 1 and 3), such exchange reactions take place in those cases where the initial titanium compound in the catalytic system does not contain a halogen and is an alkoxide, an amide, or an acetylacetonate. Thus when the AlI_3, $AlBr_3$, and $AlCl_3$ additives are introduced into the $Ti(acac)_3$–AlR_3 system[15], the contents of the 1,4-*cis*-units in polybutadiene are 72, 64, and 53% respectively. These results confirm yet again the occurrence of exchange processes and the appearance of a halogen at the titanium atom in the active centre. Judging from the microstructure of polybutadienes[15], the exchange reactions leading to the formation of catalytic complexes based on titanium trihalides do not go to completion. One cannot rule out the simultaneous presence in the system of active centres of different types, particularly in the presence of $AlBr_3$ and $AlCl_3$, which can be inferred from the somewhat high number of 1,2-units in the polymer, characteristic of active centres formed on the basis of titanium compounds with a Ti–O bond.

For a titanium system ensuring a 1,4-*trans*-polymerisation of butadiene and isoprene, the presence of a halogen in a particular component is also obligatory. One should not the $TiCl_4$–AlR_3(Al : Ti > 2), α-, γ-, and δ-$TiCl_3$–AlR_3, and $TiCl_2$–AlR_3 systems, which are highly stereospecific in the *trans*-polymerisation of butadiene and isoprene. However, the appearance of such isotypical regulating capacity regardless of the nature of the monomer is by no means observed in all cases. Thus the $Ti(n\text{-}OR')_4$–$AlRCl_2$ (Al : Ti = 10) system leads to the formation of crystalline 1,4-*trans*-polybutadiene, whereas polyisoprene containing only 38% of the 1,4-*trans*-units is formed under the same conditions[16]. With decrease of the Al : Tl ratio to 4–6, the above system becomes *cis*-regulating in relation to isoprene and yields polybutadiene with a mixed microstructure.

Data on the chemical analysis and X-ray diffraction of the products of the reaction between $Ti(n\text{-}OR')_4$ and $AlRCl_2$ showed that, for Al : Ti = 4, the insoluble component consists almost entirely of β-$TiCl_3$ crystals[16]. NMR data have led to the conclusion that the exchange reaction $Ti(OR')_4 + AlRCl_2 \rightarrow TiCl_4 + AlR(OR')Cl$ takes place in the homogeneous phase and precedes the reduction of titanium. The EPR spectrum of the reaction mixture in which insoluble compounds have already been formed shows a broad signal with a *g*-factor of 1.959, which has been attributed to titanium(III) chloride with an adsorbed aluminium alkyl. Consequently, active centres identical in their structure to those in the $TiCl_4$–AlR_3. .(Al : Ti ≅ 1) catalytic system are formed in the $Ti(n\text{-}OR')_4$–$AlRCl_2$ system with the ratio Al : Ti ≅ 4. This is also supported by the microstructures of polybutadiene and polyisoprene formed in such cases.

An unusual feature of the $Ti(OR')_4$–$AlRCl_2$ systems consists in the dependence of their stereospecificity and the nature of the group OR' and the solvent[34]. Titanium tetraalkoxides with both linear and branched primary substituents form *cis*-regulating systems regardless of the nature of the solvent, while titanates with tertiary substituents lead to the formation of *trans*-polyisoprene. The most interesting results have been obtained for titanates with secondary substituents: *cis*-polyisoprene is formed in aliphatic solvents, while the use of aromatic solvents results in the inversion of the stereospecificity and the formation of *trans*-polyisoprene. The results of the study of these systems in various solvents by EPR have been interpreted[34] as evidence for the formation of crystalline α- or β-modifications of $TiCl_3$, because the structure of the titanates in solution (monomeric or polymeric form) is influenced both by the structure of the substituent OR' and by the nature of the solvent[62]. In all cases where the initial alkoxide has the polymeric form, 1,4-*cis*-polymerisation takes place and the monomeric alkoxides lead to the formation of 1,4-*trans*-polyisoprene. The Ti–Ti bonds are shorter for the polymeric form of the alkoxides and it is believed[34] that, after the reaction with $AlRCl_2$, the difference is maintained, which is consistent with various modifications of $TiCl_3$ in which the distances between the titanium atoms are 3.54 and 2.91 Å for the α- and β-forms respectively[63]. In other words, the "seed" for the formation of the α- and β-forms of $TiCl_3$ is already present in the initial solution of the alkoxide and predetermines the stereospecificity of the $Ti(OR')_4$–$AlRCl_2$ catalyst.

Presumably analogous $TiCl_3$ formation reactions occur also in the $Ti(NR'_2)_4$–$AlRCl_2$ systems[24].

The presence of a halogen at the titanium atom is not always obligatory for the formation of a polydiene having a predominantly 1,4-structure. Thus 1,3-pentadiene gives rise to an isotactic polymer containing mainly 1,4-*cis*-units in the presence of the $Ti(OR')_4$–AlR_3 systems[50]. On the other hand, the use of a titanium halide does not always ensure the formation of 1,4-polydiene either. The polymerisation of 4-methylpenta-1,3-diene in the presence of the $TiCl_4$–AlR_3 or α-$TiCl_3$–AlR_3 systems leads to the formation of a crystalline polymer having the 1,2-structure; the $Ti(OR')_4$–AlR_3 system likewise gives rise to the 1,2-polymer but this is amorphous[64].

Thus, while there is an abundance of different varieties of highly stereospecific titanium systems, the set of active centres formed (not only as regards the selectivity of their action but also their composition and structure) is apparently much narrower. The results which might have confirmed directly the identity of active centres in many systems are so far not available. Nevertheless data on the microstructures of polydienes, the interaction of the system components, and the compositions of the corresponding products justify this conclusion. The data accumulated on various titanium systems confirm yet again the view[65] that there are no "specialised" atoms or groups responsible for the stereospecificity in the polymerisation of dienes in the presence of metal complex catalysts. Because of this, catalytic systems in fact manifest a wide variety of stereoregulating capacities, particularly when the monomer is varied. This feature hinders significantly the search for ways of regulating the stereospecificity of these catalysts. Nevertheless, certain characteristics can be traced fairly clearly. In the first place this concerns the influence of halogens on the stereospecificity.

The nature of the halogen in the $TiHal_4$–AlR_3 systems determines the microstructure of polybutadiene: the content of *cis*-units is a maximum for iodine-containing systems and a minimum for fluorine-containing systems. The decrease in the number of *cis*-units is then caused by the increased amount of *trans*-structures, while the fraction of 1,2-units hardly changes. The stereoregulating capacity of monohalide derivatives of tetrabenzyltitanium also depends on the nature of the halogen. As in systems of the Ziegler type, the maximum number of *cis*-units are formed in the presence of iodine-containing derivatives (Table 2). However, in this case the decrease of the number of *cis*-units in the macrochains corresponding to the series of iodine-, bromine-, and chlorine-containing catalysts occurs primarily due to the increase of the fraction of 1,2-units. The absence of a halogen in titanium derivatives with a Ti–C bond (Table 2) leads to the formation of a polymer in which 1,2-units predominate

and, as can be seen from the microstructure of polybutadiene obtained in the presence of $(ClC_6H_4-CH_2)_4Ti$,[43] the preferential 1,2-combination of units requires the obligatory presence of the Ti–Hal bond. The introduction of chlorine into the aromatic ring also alters significantly the stereoregulating capacity of tetrabenzyltitanium. The results obtained in the polymerisation of butadiene in the presence of systems of the Ziegler type based on $TiCl_2(OCOCCl_3)_2$ and $TiCl_2(OCOCF_3)_2$ are also consistent with this[14]. The contents of the *cis*-units in the polymer are then 60 and 38% respectively, while the number of 1,2-units remains at the same level. Thus the halogen has an appreciable influence on the stereoregulating capacity of the catalyst by altering the electron density on titanium also when the latter is part of the titanium component but is not directly involved in a Ti–Hal bond.

One must note that the influence of the nature of the halogen on the stereospecificity of titanium systems in the polymerisation of butadienes differs somewhat from that in systems with other transition metals (V, Cr, Co, Ni, Mn, Fe). The effects of these metals (M) have been compared in the $M(acac)_n-AlR_3-AlX_3$ (X = Cl, Br, or I) systems; the content of 1,4-*cis*-units in polybutadiene increases in all cases, except for titanium, in the sequence Cl > Br > I, other conditions being equal[15]. It was established[15] that the content of 1,4-*cis*-units in polybutadiene obtained in the presence of titanium systems decreases linearly with increasing electron affinity (*eV*) of the halogen present in the system. In compounds of other metals (V, Cr, Co, Ni) a direct relation is observed between *eV* and the content of units with the *cis*-structure in polybutadiene. The unusual behaviour of titanium has also been noted[66] in the study of the NMR spectra of halide derivatives of biscyclopentadienyltitanium: the opposite sequence was observed for the halogens when the apparent energies of the abstraction of electrons from the titanium atom were estimated.

The data presented in Table 6 confirm that the influence of the halogen on the stereospecificity of ionic-coordination systems is varied and is determined by the nature of the transition metal. Only the stereospecificity of systems based on *f* elements is independent of the nature of the halogen.

Table 6. The influence of the nature of the halogen on the stereoregularity of the polybutadiene obtained in the presence of catalytic systems containing halogeno-derivatives of *d* and *f* elements.

Halogen	Content of 1,4-*cis*-units				
	Ti	Co [67]	Ni [67]	Nd [68]	U [69]
F	35	93	98	95.7	—
Cl	55	98	85	96.2	99.0
Br	85	91	80	96.8	98.5
I	95	50	10	96.7	98.5

Note. The microstructure of polybutadiene obtained in the presence of the $TiHal_4-AlR_3$ systems is indicated in accordance with the data in Table 1.
The numbers in square brackets denote references (Ed. of Translation).

Sharp differences between the microstructures of the polymer have not been observed as a function of the halogen in the polymerisation of isoprene in the presence of titanium systems of the Ziegler type. However, in the presence of tetrabenzyltitanium monohalide derivatives (Table 4) the overall variation of the number of units with the *cis*-structure in polyisoprene on passing from iodine-, to bromine-, and chlorine-containing derivatives is consistent with the relation observed in the polymerisation of butadiene in the presence of the same compound.

The replacement of the halogen atoms in $TiHal_4$ by substituents of another chemical type alters significantly the stereoregulating capacity of the catalytic systems. Individual examples of this are presented in Tables 1, 3, and 5. The replacement of the Ti–Hal bonds in the titanium component by Ti–O bonds increases the contribution of the 1,2-addition in polybutadiene. Thus the contents of the 1,2-units in the polymers for systems based on $TiCl_4$, $TiCl_2(OCOCH_3)_2$, and $TiCl(OCOCH_3)_3$ are 14, 21, and 42% respectively[14]. The same type of variation is manifested in the $TiCl_4$, $TiCl_2 \cdot (OC_4H_9)_2$, and $Ti(OC_4H_9)_4$ series—14, 48, and 73% of 1,2-units respectively[14]. A sharp decrease in the rate of polymerisation is observed in the series indicated. The step involving the addition of 1,2-units takes place approximately 300 times more slowly than for the 1,4-*cis*-units, which is indicated by a comparison of the rate constants for the chain propagation of polybutadiene when catalytic systems based on $Ti(OR')_4$ and TiI_2Cl_2 are used[70].

Data obtained for systems based on dichloroacetoxytitanium derivatives have shown that the content of 1,4-*cis*-units in polybutadiene diminishes with increase of the electronegativity of the acido-ligand[14]. An analogous picture has been noted also for titanium dichloride derivatives containing the anions of butyric acid or its chloro-derivatives. In all these cases the content of 1,4-*cis*-units diminishes due to the formation of *trans*-structures, while 1,2-addition in the chain is maintained at the same level regardless of the presence and nature of the halogen in the acido-ligands.

Presumably the change in the chemical nature of the substituents at the transition metal atom (and not the accompanying steric factors, which nevertheless must be taken into account) have in fact the primary influence on the catalytic characteristics of the active centres. Thus an increase in the length or bulk of the substituent of one chemical type at the titanium atom does not affect the stereospecificity of the catalyst[14,70]. It has been shown for the $Ti(OR')_4-AlR_3$ systems[70] that, when the substituents R' are varied within a homologous series, the microstructure of polybutadiene and the rate constant for chain propagation do not vary. The reactivity of the active centres is maintained, but the reactivity of the systems diminishes with increase in the size of R' as a result of the decrease of the number of these centres, the latter being related primarily to the steric hindrance in the interaction of the components of the catalytic system.

In considering the possibility of regulating the stereospecificity of catalytic systems of the ionic coordination type, one must also deal with results obtained in the study of these systems in the presence of modifying electron-donating additives. The nature of the variation of the stereospecificity of Ziegler systems following the introduction of an electron donor is determined by the nature of the transition metal. It has been shown for the $M(acac)_n-AlR_2Cl$ (M = V, Cr, Co, Ni, Ti) systems[19] that the influence of bases is most notable for the titanium systems; the extent of the changes in the microstructure is smallest when bases are introduced into a nickel-containing system.

The introduction of ethers, thioethers, and tertiary amines into the highly stereospecific *cis*-regulating TiI_4-AlR_3 system impairs the microstructure of polybutadiene as a result of the increase of the content of the 1,4-*trans*-unit, while the number of 1,2-units hardly changes[71,72]. The influence of ethers on the microstructure of the polymer varies in the sequence dimethyl ether > ethyl methyl ether > diethyl ether > dibutyl ether, which agrees with the variation of the capacity of the ethers for complex formation. A similar picture has been

observed also after the introduction of electron donors into another *cis*-regulating system: $TiCl_4$–AlI_3–$AlHCl_2OR_2$.[9] The content of the *trans*-units in polybutadiene reaches 80% (without change in the content of the 1,2-structures) when amines are introduced into the $TiCl_4$–AlR_3 system[73], which gives rise to a polymer with a mixed microstructure in the absence of these additives. With the aid of electron donors, it is sometimes possible to achieve the almost complete inversion of the stereospecificity of the catalyst. Thus the addition of tetrahydrothiophen to the $TiCl_3.3AlI_3$–AlR_3 system leads to the formation of polybutadiene containing 88% of the 1,4-*trans*-units, while in the absence of a Lewis base the system exhibits a high *cis*-regulating capacity[74].

The addition of electron donors to systems based on titanium halides does not alter the ratio of the sums of 1,4-units and 1,2-units in the polybutadiene chain but drives the process towards a more intense formation of the 1,4-*trans*-units. On the basis of the concept of the *anti–syn* isomerisation of the terminal unit[75], it has been suggested that bases displace the equilibrium towards the formation of the *syn*-complex responsible for the appearance of units with the *trans*-structure in the chain.

The influence of the structure of the electron donors on the stereospecificity of the $TiCl_4$–AlR_2 systems in the polymerisation of isoprene has been traced[76] in relation to a series of tetra-alkyldiamines and, by altering the amount of *N,N,N',N'*-tetramethyldiamino-4,4'-diphenylmethane, it has been possible to regulate smoothly the stereospecificity of the system.

In contrast to the *cis*-regulating halogen-containing titanium systems of the Ziegler type, the addition of electron donors to tribenzyltitanium iodide in toluene enriches polybutadiene in the 1,2-units and polyisoprene in the 3,4-units[40,47].

Table 7. Dependence of the stereospecificity of systems based on titanium tetrachloride on the nature of the cocatalyst in the polymerisation of isoprene.

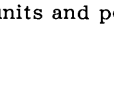
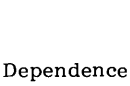
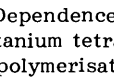
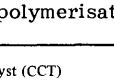
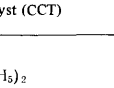
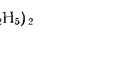
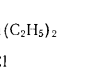
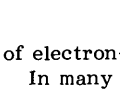
Cocatalyst (CCT)	CCT : $TiCl_4$	1,4-*cis*-units, %	Refs.
AlR_3	⩾1	95—99.5	[1, 6, 26, 27]
$AlH(Hal)_2 \cdot O(C_2H_5)_2$	1.5—2.2	95—96	[77]
$AHCl_2 \cdot NR_3$	1.4—1.7	95—96	[78]
$AlH_2Cl \cdot NR_3$	0.5—0.6	96	[78]
$AlH_3 \cdot NR_3$	0.35—0.5	94—95	[78]
$AlH_2(NR_2)$	0.55—0.7	95—96	[78]
$AlH_2(OR) \cdot N(CH_3)_3$	0.6—0.7	94—96	[78]
Polyiminoalanes	1.4—1.8	94—96	[79, 80]
AlR_2F	2—50	96	[81]
$[Ca(C_2H_5)_2]_n \cdot Zn(C_2H_5)_2$	0.6—1.5	95—96	[82]
R_2SnH	⩾1	95—97	[83, 84]
$R_3SiOR'—AlR_2''Cl$	0.5—1	97	[85]
$R_3SnH—AlR_2'Cl$	0.5—6.0	97	[86]
$R_3SnH—AlBr_3$	2—4	95.4	[87]
CdR_2	0,5	90	[88]
AlB_3H_{12}	0.7—1.5	80	[89]
MgR_2	0.8	75	[90]

2. The Influence of the Nature of the Organometallic Component on the Activity and Stereospecificity of the Catalyst

Mainly organic derivatives of Group I–III metals are used as the organometallic components (cocatalysts) in Ziegler systems. Despite the wide variety of cocatalysts, organoaluminium compounds (OAC) are most widely used in the polymerisation of butadiene and isoprene. Although the presence of a cocatalyst is not always obligatory for the occurrence of ionic-coordination polymerisation, it can have a significant influence on the process characteristics.

The microstructure of the polyisoprene obtained in the presence of titanium tetrachloride (Table 7) does not depend significantly on the nature of the organometallic compound, *cis*-polymerisation occurring in all cases. A distinctive feature of systems based on the OAC is their high catalytic activity combined with a high stereoregulating capacity (Tables 7 and 8).

Table 8. The influence of the nature of the organoaluminium compound on the microstructure of polydienes ($TiCl_4$ and TiI_2Cl_2 catalysts for isoprene and butadiene respectively)[91].

No.	OAC	Content of 1,4-*cis*-units, %	
		polybutadiene	polyisoprene
1	Al (iso-C_4H_9)$_3$	91	95
2	Al (C_7H_{15})$_3$	90	96
3	Al ($C_{10}H_{21}$)$_3$	90	96
4	Al ($C_{15}H_{31}$)$_3$	91	96
5		90	96
6		90	95
7		92	96
8		92	95
9		—	97
10		91	96
11	OAC based on 1,2-polybutadiene	92	96
12		92	97
13	(iso-C_4H_9)$_2$Al—N (C_2H_5)$_2$	93	96
14		92	—
15		91	—
16		92	97
17	(iso-C_4H_9)$_2$Al—C≡C—C_6H_5	92	96

The role of electron-donating additives has been adequately elucidated. In many cases they (for example, water and alcohols) can react both with the transition metal compound and with the organometallic cocatalyst. On the other hand, the main cause of the effect of bases on the stereospecificity of the system is probably associated with their ability to be coordinated to the transition metal atom, to alter its ligand environment (electron density), and consequently to influence the reactivity of the active centre.

Aluminium tetrahydroborate and organomagnesium compounds are least stereospecific as cocatalysts in the polymerisation of isoprene. In their presence, low-molecular-weight polymers containing not more than 80% of *cis*-units are obtained. The polymerisation of butadiene in the presence of TiI_4, TiI_2Cl_2, and organomagnesium cocatalysts[92,93] involves the formation of polymers whose stereoregularity is as high as that of the polymers obtained using AlR_3. Organosilicon and organotin compounds occupy a special place among cocatalysts

(Table 7). They permit the use of a wide range of component ratios of the catalytic system, but the molecular weight of the polymers is low. Cocatalysts based on polyiminoalanes $[-AlH-NR-]_n$ [60] cause a rapid polymerisation of the diene and the polymers obtained under these conditions exhibit a high stereoregularity and have high molecular weights and a low content of the gel fraction. The activity of polyiminoalanes as cocatalysts in the polymerisation of isoprene in the presence of $TiCl_4$ depends on the structure of the group R, the greatest activity being attained for groups with a secondary carbon atom in the α- or β-position relative to the nitrogen atom.

More detailed data are available concerning the influence of the structure of the OAC on the characteristics of the catalytic systems for the polymerisation of dienes. In the first place one should note that a change in the structure (chain length, degree of branching, degree of cyclisation, and degree of unsaturation) of the hydrocarbon groups in AlR_3 does not entail a change in the stereospecificity of the catalytic system (as shown in experiments using titanium halides and tetraalkoxides[91,94–97]). The replacement of alkyl groups by groups containing heteroatoms (N, O, Si) is also not reflected in the microstructure of polydienes (Table 8). However, in contrast to their stereoregulating capacity, the activity of titanium systems in the polymerisation of both butadiene and isoprene depends significantly on the structure of the group in the organoaluminium component. The following main characteristic features have been discovered.

With increased length of the alkyl group within the limits of the homologous series of the OAC, the rate of polymerisation initially rises and then tends (Fig. 1) to a limiting value for OAC in which the chain length of the group exceeds C_{12}.[91,94–97] Here the region of catalytic activity shifts (Fig. 2) towards higher Al : Ti ratios with increase in the size of R.[91,96,97] AlR_3 with branched alkyl groups are more reactive than those with linear groups. However, among OAC with substituents having the iso-structure the activity also increases with increase of the number of carbon atoms in the group[94].

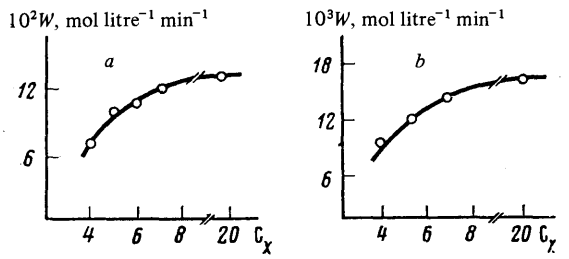


Figure 1. Dependence of the rate of polymerisation W of butadiene in the presence of TiI_2Cl_2–AlR_3 (*a*) and isoprene in the presence of $TiCl_4$–AlR_3 (*b*) on the number of carbon atoms C_X in the alkyl group R; solvent–toluene; t = 20 °C; $[TiI_2Cl_2] = 1.5 \times 10^{-3}$ M; $[TiCl_4] = 2.7 \times 10^{-3}$ M; $[C_4H_6]$ = 0.82 M; $[iso\text{-}C_5H_8]$ = 1.0 M.[91]

For the same number of carbon atoms, the rate of polymerisation is higher for aluminium trialkyls with linear substituents than for AlR_3 with cyclic substituents. With increase of the bulk of the cyclic substituent, the activity of the system falls. For the same number of carbon atoms in R, the rate of polymerisation is higher for AlR_3 with double bonds in the group than for saturated substituents, the presence of conjugated double bonds resulting in a still greater increase in the rate (Fig. 3).[91,97]

The replacement of alkyl groups in AlR_3 by substituents containing heteroatoms (N, O, Si) decreases the activity of the catalytic systems[91,97]. Consequently the increase in the activity of the titanium catalytic systems suggest the usefulness of employing organoaluminium compounds containing 8–10 carbon atoms in the hydrocarbon substituents and double bonds, in particular conjugated double bonds. It may be hoped that, when gel-immobilised OAC are used, it will be possible to increase still further the activity of the catalysts while retaining their high stereospecificity, particularly since a recent communication[98] confirms this possibility.

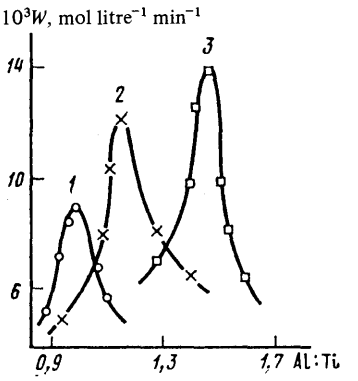


Figure 2. Dependence of the rate of polymerisation of isoprene on the Al : Ti ratio in the $TiCl_4$–AlR_3 systems with R = iso-C_4H_9 (curve *1*), n-C_7H_{15} (curve *2*), and n-$C_{10}H_{21}$ (curve *3*); solvent—toluene; $[TiCl_4] = 2.7 \times 10^{-3}$ M; [monomer] = 1.0 M; t = 20 °C.[91]

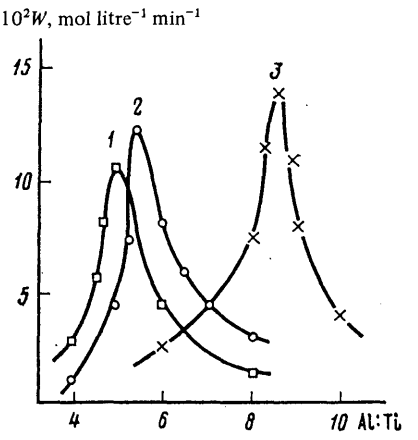
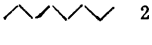
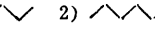
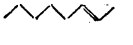


Figure 3. Dependence of the rate of polymerisation of butadiene in the presence of the TiI_2Cl_2–AlR_3 systems with different Al : Ti ratios on the structure of the group R:

1)  2)  3) 

solvent—toluene; t = 20 °C; $[TiI_2Cl_2] = 1.5 \times 10^{-3}$ M; [monomer] = 0.82 M.[91]

Thus, when substituents at the aluminium atom in the cocatalysts are varied within the limits of a homologous series, the stereospecificity of ionic-coordination systems remains constant in the polymerisation of dienes, but their activity changes, as in the case where substituents are varied similarly at a transition metal atom. Such variation results in the formation of active centres with identical structures and reactivities. This is supported, apart from the microstructure data, by the following facts. The form of the EPR spectra of the reaction product in the TiI_2Cl_2–AlR_3 and $Ti(OR')_4$–AlR_3 systems is independent of the length of the group R.[96] The activation energy for the chain propagation reaction is likewise independent of the length and structure of the hydrocarbon group in the polymerisation of isoprene in the presence of $TiCl_4$–AlR_3 and amounts to 5–6 kcal mol^{-1}.[91,99] All the changes in the activity of the catalytic systems associated with the differences between the structures of the substituent in the OAC and unaccompanied by a change in the microstructures of the polymers are due to the different concentrations of the active centres, while the reactivity of these centres (k_p) remains unchanged (Table 9).

Table 9. The influence of the structure of AlR_3 on the rate constant for the propagation reaction (k_p), the content of active centres (C_a), and the constant for chain transfer to AlR_3 (k_o^{Al}) in the polymerisation of butadiene and isoprene in the presence of the titanium-containing $TiHal_4$–AlR_3 systems (solvent—toluene; t = 25 °C).[97]

Reaction conditions	AlR_3	$10^{-3}k_p$, litre mol^{-1} min^{-1}	$C_a/C_{Ti}\cdot10^2$	$10^{-3}k_o^{Al}$ litre mol^{-1} min^{-1}
TiI_2Cl_2; Al:Ti = 7, butadiene	Al (iso-C_4H_9)$_3$	7.4	1.5	3.4
	Al (–C_2H_4– )$_3$	7.4	3.6	1.5
$TiCl_4$; Al:Ti = 1.1; isoprene	Al (iso-C_4H_9)$_3$	1.0	0.3	0.2
	Al (–C_2H_4– )$_3$	1.0	0.7	0.1
	Al ()$_3$	1.0	1.0	0.1

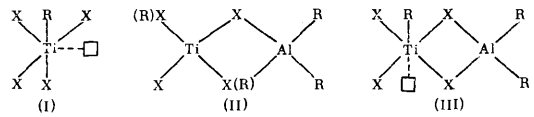
The increased molecular weights of the polydienes when higher AlR_3 are used are associated with the increase of the macrochain propagation time as a result of the decrease of the constant for chain transfer to AlR_3 with increase in R (Table 9).

III. THE STRUCTURE OF ACTIVE CENTRES AND THEIR STEREOREGULATING CAPACITY

The study of the mechanism of the stereospecific polymerisation of dienes is related directly to the structure of the active centres.

It is generally accepted that polymerisation involves the transition metal–carbon bond and that the cocatalyst plays the role of a complex-forming agent, a reductant, and an alkylating agent. However, the question whether or not the organometallic compound is incorporated in the composition of the active centre for polymerisation, i.e. the question of the mono- or bi-metallic structure of the active centres, still remains controversial.

There exists a view[100–103] that the active centre (I) includes only the alkylated transition metal compound. However, this structure of the active centre does not explain the influence of the nature of the organometallic compounds on the stereospecificity of the catalytic systems.



□ - vacant site, X-ligand, R-alkyl group

The bimetallic structure of the active centres (II) presupposes an important role of the organometallic compounds in their creation[104–107], a more important role than simple stabilisation of the alkylated transition metal compound via halide bridges[108,109]. Thus Minsker and co-workers[106,107,110] demonstrated by quantum-chemical calculations the high probability of the propagation of the polymer chain with participation of the $\overset{-}{Al}$–R–$\overset{\delta+}{Ti}$ group, while Cossee's mechanism[101,102] presupposes chain propagation solely via the Ti–R bond. It is believed[106,107,110] that the OAC coordinated to the titanium compounds is directly involved in the addition of the monomer to the growing chain via the simultaneous electrophilic (from the side of the Ti atom) and nucleophilic (from the side of the Al atom) attack on the monomer.

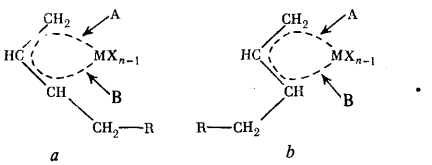
In conformity with the schematic representation of the active centre (III), the propagation of the polymer chain takes place at the transition metal, while the aluminium compound is one of the ligands of the transition metal[111–113]. According to Avdeev et al.[112], the OAC, present in the second coordination sphere of the transition metal, cannot influence appreciably the reactivity of the active centre in this case. Thus the third type of active centres, where the leading role of the transition metal compound is assumed, also takes into account the appreciable role of the OAC in the formation and stabilisation of the active centres. Active centres of type (III) made it possible to explain[114] why the reactivity of the active centres is independent of the nature of the OAC in the ionic-coordination polymerisation of α-olefins. Our set of investigations[91,97,99], using a large number of aluminium trialkyls of different structures, showed that active centres of type (III) are most probably formed also in the polymerisation of dienes, since the reactivity of the active centres of titanium systems is independent of the structure of the organoaluminium component.

Although the hypothesis that the structure of the active centres in the polymerisation of dienes is modelled by the π-allyl complexes of transition metals is generally accepted, the question of the causes of stereoregulation, i.e. of the factors responsible for the formation of polydiene macrochains with 1,4-*cis*-, 1,4-*trans*-, 1,2-, or 3,4-units remains controversial. Two concepts predominate in the literature on this topic.

The concept of the *cis*–*trans* geometrical control[115–117] takes into account the presence of two double bonds in the conjugated dienes. If the diene is coordinated to the active centre via two double bonds, then its subsequent incorporation in the growing chain entails the formation of a unit with the 1,4-*cis*-configuration. For the monodentate coordination of the diene, it is possible to obtain polymers containing 1,4-*trans*- or 1,2-units. Thus the coordination of the monomer and hence the stereoregularity of the polymer depend on the matrix effect of the catalyst. Active centres with a single vacancy (a single coordination site), for example α-$TiCl_3$, permit the possibility of employing only one double bond of the diene in the *S*-*trans*-form, while on centres with two vacancies (for example, the crystal lattice of β-$TiCl_3$), the diene molecules can be coordinated using either one or

two double bonds (the *S-cis*-form)[118]. Furukawa[65] suggested that the microstructure of the polydienes, determined by the mode of coordination of the monomer, depends on the electron density at the transition metal atom. The probability of the mono- and bi-dentate coordination of the monomer is determined, according to Furukawa[119], by the difference between the energy levels of the orbitals of the transition metal involved in bonding with the π-orbitals of the diene and the highest occupied orbitals of the latter. In conformity with the proposed mechanism, 1,4-*cis*-polydienes are obtained when the energy levels of the bonding orbitals of the metal and the highest occupied orbitals of the monomer are close to one another; when there is a large difference between the energy levels, polymers with the 1,2- or 1,4-*trans*-structures are formed. The electronegativity of the ligands, which influences the positions of the energy levels of the transition metal orbitals, is an important stereoregulation factor.

According to the other concept, the stereoregularity of the polymer chain is determined by the π-alkenyl polymer–transition metal linkage and not the coordination of the monomer to the active centre, *the* anti-form *a* corresponding to *cis*-addition and the *syn*-form *b* corresponding to the *trans*-units:



a *b*

It is believed[116,119] that the *anti–syn* orientation should depend on the coordinating capacity of the double bond adjoining the π-alkenyl linkage at the end of the macromolecule (i.e. on the penultimate double bond), while the geometrical configuration of the π-alkenyl end of the growing chain is unimportant. However, the stereospecificity of the action of the catalyst has been attributed[75,120–125] to the configuration of the π-alkenyl unit of the growing chain. This version is supported by data obtained in a study[126] where it was shown by ^{1}H NMR that there is only a very slight possibility of the coordination of the penultimate double bonds of the growing chain.

According to a number of investigations[75,122,124,125], a conjugated diene always behaves as bidentate ligand, which is favoured by energy factors for conjugated dienes, and the primary steps involving the addition of the monomer therefore lead solely to the *anti*-configuration of the π-alkenyl centre. The content of the 1,4-*cis*- or 1,4-*trans*-structures is determined by the ratio of the rates of chain propagation and *anti–syn* isomerisation of the active centre: a higher rate of chain propagation results in the formation of a polymer with the 1,4-*cis*-structure of the units on insertion of the monomer in the π-alkenyl linkage of the *anti*-complex formed initially, while at low rates of chain propagation the role of the *anti–syn* isomerisation reaction of the active centres increases and the thermodynamically more stable *syn*-π-complexes, giving rise to units with a 1,4-*trans*-structure, are formed. Such interconversions of the structures take place fairly readily for simple compounds[127]; the *anti–syn* isomerisation of the π-alkenyl complexes of certain transition metals has been observed also in the polymerisation of dienes[128–131], the rate of reaction depending on the structure of the alkyl substituent in the diene.

The coordinated diene molecule can enter the growing chain either from side A, whereupon polymer chains with 1,4-units are formed, or from side B, which leads to the formation of polymers with a 1,2-structure of the units.

Very little is known about the factors directing the stereospecific polymerisation towards the formation of the 1,4- or 1,2(3,4)-polymer, nevertheless experimental data show indirectly that these factors may depend both on the monomer and on the catalyst. Thus comparison of the results of the polymerisation of butadiene and 4-methylpenta-1,3-diene in the presence of α-$TiCl_3$–AlR_3 showed[132] that in both cases the monomer is inserted in the same Ti–C bond of the π-allyl complex at the end of the chain, which contains the least substituted and hence the most reactive carbon atom. However, this approach cannot explain the formation of 1,2-polybutadiene. On the grounds that in the majority of polybutadienes in which the 1,2-units predominate, including those obtained in the presence of $Ti(OR')_4$–AlR_3, the residual units have almost exclusively the 1,4-*cis*-structure, the authors[132] believe that the monomer in these systems is always coordinated as a bidentate ligand and the π-allyl complex at the end of the chain has the *anti*-structure. However, in such systems one assumes a geometry of the catalytic complex such that the terminal, carbon atom of the coordinated monomer can be closer (at a distance equal to a single bond length) to the more substituted although less reactive third carbon atom in the π-allyl group. As a result of this, the monomer is inserted preferentially in the B direction and 1,2-polybutadiene is formed.

This approach, which takes into account the rigorously steric, geometrical characteristics of the active centre, should apparently be regarded as useful. Indeed the presence of bulky substituents at the titanium atom promotes in all cases and, what is most important, independently of their chemical nature the appearance of 1,2-units in the polybutadiene chain. The greater the number of such ligands at the titanium atom, the larger the fraction of 1,2-junctions. This is indicated by the results of the polymerisation of butadiene in the presence of catalytic systems consisting of $Ti(OR')_4$,[25,70] $Ti(NR_2)_4$,[24] $TiCl_2(indenyl)_2$,[14] $TiCl_2(fluorenyl)_2$,[14] $TiCl_2(OR')_2$,[14] and $TiCl_2(OCOR')_2$ [14] in combination with AlR_3.

The causes of the formation of a polymer with a mixed microstructure can be accounted for also by factors other than the *anti–syn*-isomerisation of the active centre, a difference in the modes of incorporation of the monomer in the growing chain, or an alteration of the geometry of the catalytic complex. The question whether the polymerisation involving the formation of polydienes with a mixed microstructure occurs on the same active centres or on non-identical active centres with different activities and stereospecificities still remains open. The latter possibility is not ruled out if only because even when the Al : Ti ratio is altered only slightly in systems based on titanium halides, the microstructure of the polydienes begins to change. Unfortunately, there are almost no literature data which would make it possible to follow the qualitative and quantitative variation of the active centres as a function of the component ratio in catalytic systems. Thus it has been shown in a study[133] of the polymerisation of butadiene in the presence of TiI_4–$Al(iso\text{-}C_4H_9)_3$ that the propagation rate constant increases sharply when the Al : Ti ratio is raised from 1.5 to 5.5, but a clear-cut correlation between the concentration of active centres and the Al : Ti ratio was not found.

Nevertheless, certain results can be interpreted only on the assumption of the simultaneous presence in a particular system of active centres of different types and with different reactivities. Thus the separation of the products of the polymerisation of butadiene in the presence of $TiCl_4$–AlR_3 by extraction with different solvents made it possible to isolate from the overall reaction mass a highly stereoregular 1,4-*cis*-polybutadiene[134]. In the polymerisation in the presence of β-$TiCl_3$ the formation of two polymers separable by extraction (1,4-*cis*-, and 1,4-*trans*-polybutadienes) in comparable

amounts was also noted[135]. Even when highly stereospecific catalytic systems such as TiI_2Cl_2–AlR_3 (monomer = butadiene) and $TiCl_4$–AlR_3 (monomer = isoprene) were used, an increase of the content of the 1,4-*cis*-units was observed in all the fractions of rubbers with increase in the molecular weight of the fraction; a particularly marked decrease of the amount of *cis*-units is observed in the region of molecular weights below 20000.[27] This phenomenon is regarded as a consequence of the presence in the catalyst of different active centres with different propagation and *anti–syn* isomerisation constants, polymers with a higher molecular weight and a higher content of 1,4-*cis*-units being formed on the more active centres. It is believed[136] that EPR data confirm the hypothesis of the existence of two forms of active centres in iodine-containing titanium systems: monomeric paramagnetic centres with a high catalytic activity lead to the formation of a high-molecular-weight 1,4-*cis*-polydiene, while associated diamagnetic centres are much less reactive and the decrease of the content of the 1,4-*cis*-units in the polymer probably depends on them.

One can therefore assume that the significant difference between the stereoregulating capacities of the $TiCl_4$–AlR_3 system ($Al:Ti \geq 1$) in the polymerisation of butadiene and isoprene is due to the fact that in the case of butadiene the polymerisation takes place simultaneously on two types of active centres (*cis*- and *trans*-regulating), which in fact leads to a mixed microstructure of the polymer. On the other hand, the polymerisation of isoprene hardly takes place on the less active *trans*-regulating centres (if only by virtue of the steric hindrance to coordination) and the entire polymerisation process occurs on the *cis*-regulating active centres. Quantum-chemical calculations[137,138] agree with these ideas.

It is difficult to obtain experimental data on the structure and the active centres in ionic-coordination polymerisation of dienes because of their high sensitivity to impurities, the complexity of their composition, and their low concentrations. Thus the degree of conversion of the initial titanium halide into the catalytically active compounds by its reaction with AlR_3 does not exceed several per cent[70,91,97,99,133,139–142]. This parameter is even lower (<1%) for systems based on titanium alkoxides[70,143].

The lack of experimental data on the structure of the active centres is partly compensated by quantum-chemical studies. The relevant calculations have the following aspects: the nature of the metal–monomer and metal–alkyl bonds, the coordination of the monomer to the active centre, and its insertion in the metal–carbon bond. There have been almost no detailed calculations of the structure of the active centres for the polymerisation of dienes in the presence of Ziegler–Natta catalyst and of the potential energy surfaces for the addition of the diene to the active centre (of the kind carried out, for example, for α-olefins[110,112,114,144]).

Quantum-chemical calculations on the anionic polymerisation of dienes in the presence of organometallic derivatives of alkali metals modelling the structure of the terminal unit of the growing macromolecule linked to the transition metal have been published in a number of communications[145–150] and a computer study of the formation of active centres and of the mechanism of the polymerisation of α-olefins and dienes in the presence of heterogeneous Ziegler–Natta catalysts has been described[137]. According to calculations[137], the role of the organometallic compound MR consists in building up the crystal lattice of the catalyst, in the formation of a Ti–R–M bridge bond, and in the formation of an unusual structure of the active centre by the groups R and the metal atoms ("tunnel"), which has an orienting effect at the monomer coordination stage.

Attention has been concentrated in semiempirical[114] and non-empirical[151] calculations on the estimation of the electronic structures of various titanium–aluminium–olefin complexes and their alteration in the addition of the olefin to the Ti–C bond. As a rule, the choice of the model of the active centre is based on the available experimental data. Models of active centres have been obtained by the computer calculation of the random absorption of AlR_3 on the surface of $TiCl_3$ crystals in only a few studies[110,137,151]; this made it possible to predict different forms of active centres and to select the most probable.

A hypothesis concerning the mechanism of catalytic polymerisation is impossible without the elucidation of the nature of the lability of the transition metal–carbon bond. In terms of this aspect, the data of L'vovskii and Erusalimskii[152,153], who investigated the equilibrium properties and the electronic nature of the lability of the Ti–C σ-bond in a series of alkyl halide derivatives of quadrivalent titanium, are of great interest. L'vovskii used the unrestricted version of the Hartree–Fock–Roothaan (UHFR) for quantum-chemical calculations and compared it with the restricted version (RHFR) in the CNDO approximation. Calculations on the homolytic dissociation of the Ti–C bonds in $TiCl_3CH_3$ and the Al–C bonds in $AlCl_2CH_3$ by the UHFR method showed[153] that there is a very much smaller energy barrier to the dissociation of the Ti–C bond than to the dissociation of the Al–C bond. The electronic correlation has a much greater influence on the lability of the Ti–C bond and this influence is determined mainly by the properties of the *d* orbitals of the transition metal[153], which explains the difference between the energy barriers to the homolytic dissociation of the Ti–C and Al–C bonds. It is also of interest to note that calculations[153] indicate an increase of the energy barrier to the dissociation of the Ti–C bonds in the sequence $TiCl_3C_2H_5 < TiCl_3CH_3 < (\eta^5\text{-Cp})_2.TiClCH_3$, which agrees with the variation of the thermal stability of these compounds.

However, all the known calculations on reaction pathways have been carried out within the framework of the RHFR method, where, in the light of the results of L'vovskii and Erusalimskii[152,153], some caution is needed in assessing the energy barriers obtained and hence also the correctness of the choice of both the rate-limiting stage and the single- and two-stage mechanisms of chain propagation.

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The general level of the results achieved at the present time in the field of the ionic-coordination polymerisation of dienes is fairly high. Extensive experimental data have accumulated on various aspects of this field and further studies are being vigorously prosecuted. However, despite the advances made, the state of knowledge on a number of questions is still merely empirical. A particular consequence of the lack of a profound theoretical basis is that new catalytic systems are selected, as regards both composition and the formation conditions, by a purely experimental procedure. In view of the complexity of the physicochemical picture of the formation and functioning of the active centres, the characteristic features of the polymerisation of a particular diene in the presence of a given transition metal cannot always be extended to other systems and other monomers. This applies in the first place to the stereospecificity of the action of ionic-coordination systems, which is indicated by the analysis of the literature data presented in this review. On the other hand, one can assume, on the basis of modern ideas about the structure of the active centres, that the lack of an effect by the structure of the organoaluminium component on the stereospecificity of the titanium system apparently obtains

also in other systems of the Ziegler type. As regards the question of the influence of the structure of the OAC on the activity of the systems, the characteristics discovered for the titanium systems can hardly hold in all other cases in view of the wide variety of the functions of the organoaluminium compound in the Ziegler system, particularly when account is taken of their reducing and alkylating capacities.

Thus there is an evident necessity for further studies designed to accumulate new experimental facts which would serve as a basis for the development of methods for the specific control of processes involving the stereospecific polymerisation of dienes.

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Thermochemistry of Haloethanes

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Data on the thermochemistry of haloethanes are surveyed. The most reliable standard enthalpies of formation of 37 haloethanes are recommended on the basis of a critical analysis of the experimental results published up to 1980 inclusive (and partly in 1981). The constants of a computational scheme for the estimation of the enthalpies of formation of hitherto uninvestigated haloethanes have been evaluated by the method of least squares. The enthalpies of formation of 210 haloethanes containing H, F, Cl, and Br have been calculated with the aid of these constants.
The bibliography includes 131 references.

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I. INTRODUCTION

Organohalogen compounds are widely used in many branches of the national economy. The study of their thermochemical properties is of great practical and theoretical importance[1,2]. Studies[3,4] in which the available experimental data were analysed and recommendations were made concerning the estimation of the standard enthalpies of formation of hitherto uninvestigated compounds were devoted to the thermochemistry of halomethanes and also organofluorine compounds with three or more carbon atoms. No similar investigations have been published on the thermochemistry of haloethanes.

However, haloethanes occupy a very important place in modern chemistry and technology. They are used as cooling agents, aerosol propellants, flame inhibitors, solvents, etc. Some of them have found applications in medicine and as effective anaesthetics. Many representatives of the haloethanes are the final or intermediate products in large-scale manufacturing processes (CF_2ClCF_2Cl, C_2F_5Cl, CH_3CHF_2, CF_2BrCF_2Br, etc.[5]). In this connection detailed analysis of the present state of the thermochemistry of haloethanes is urgently required. Its practical value is determined primarily by the need to have reliable thermochemical data for calculations on technological processes. The study of the influence of the nature and number of substituent atoms on the energetic properties of molecules with similar compositions and structures is of theoretical interest.

There are few experimental enthalpies of formation of haloethanes and they are frequently contradictory. While the total number of known haloethanes is 630, the enthalpies of formation of only 30 compounds of this class can be found in the handbooks published in recent years[6-9]. Furthermore, the discrepancies between the values of ΔH_f° adopted from different sources (for example, for CF_2ClCF_2Cl and $CF_2Br.CHFCl$) reach up to 50–60 kJ mol^{-1}.

During recent years many new data, which have not yet been incorporated in handbooks, have been published on the enthalpies of formation of haloethanes. Thus the enthalpies of formation of 9 compounds which had not been investigated previously were determined: CH_2ClCCl_3, CH_2CF_2Cl, $CH_3CF_2.Br$, $CF_3CH_2.Br$, $CH_3CHClBr$, CH_2ClCH_2Br, $CF_3CHClBr$, $CF_2.ICF_2I$, CH_3CF_2I. The enthalpies of formation of certain substances for which previous data had been contradictory were redetermined (CF_2ClCF_2Cl, $CF_2ClCFCl_2$, $CF_2BrCHFCl$). Significant errors in the results of previous studies were discovered and eliminated in these measurements. New determinations of the enthalpies of formation of certain haloethanes (CH_3CH_2Cl, CH_3CHCl_2, $CH_2ClCHCl_2$, $CHCl_2CHCl_2$) made it possible to revise previous recommendations.

In addition the values of ΔH_f° for a whole series of haloethanes should be recalculated and significantly modified because their calculation involves the use of the ΔH_f° for compounds whose values have been fundamentally redetermined in recent years. For example, a new determination of the enthalpy of formation of chlorotrifluoroethylene[10] led to a sharp change in the values of ΔH_f° for CH_2FCHF_2 and $CF_2.BrCFClBr$, which were calculated from the enthalpies of hydrogenation[11] and bromination[12] of $CF_2=CFCl$. Certain enthalpies of formation of substances in the gaseous state have been revised as a result of new determinations of the enthalpies of vaporisation.

The publication in recent years of a large number of experimental ΔH_f° makes it timely and necessary to re-examine the set of enthalpies of formation of haloethanes. This paper surveys the present state of the thermochemistry of haloethanes. The methods of experimental determination and the possibility of the approximate calculation of the enthalpies of formation of haloethanes are briefly characterised. All the available experimental literature data for the ΔH_f° for haloethanes published up to 1980 inclusive (and partly in 1981) are examined and analysed. The most reliable ΔH_f° for 37 compounds are recommended on the basis of this analysis. The enthalpies of formation of all the 210 possible bromochlorofluoroethanes have been calculated by Bernstein's method[13,14] from the selected experimental ΔH_f° for haloethanes containing H, F, Cl, and Br atoms. The inadequate number of experimental enthalpies of formation of iodoethanes at present precludes a similar calculation for all haloethanes including the iodo-derivatives.

II. UNITS OF MEASUREMENT AND KEY AND AUXILIARY QUANTITIES

In conformity with the International System of Units ("SI"), all the thermodynamic quantities in the present review are expressed in joules. The initial data and the data in handbooks expressed in kcal were recalculated on the basis of the relation 1 cal = 4.1840 J.[15] The atomic weights were adopted

in accordance with a IUPAC publication[16]. The enthalpies of formation of haloethanes were calculated using the following ΔH_f° (kJ mol^{-1})[17] included in the unique system of key quantities adopted by the Committee on Numerical Data for Science and Engineering (CODATA):

Compound	CO_2 (gas)	H_2O (liq.)	F^- (aq.)	Cl^- (aq.)	Br_2 (gas)
ΔH^0_f	−393,51±0,13	−285.830±±0.042	−335,35±0.65	−167,08±0,088	30.91±0,11
Compound	I_2(gas)	HCl (gas)	HBr (gas)	HI (gas)	
ΔH^0_f	62.421±0.08	−92,31±0,13	−36,38±0,17	26,36±0.8	

All the values of ΔH_f° indicated in this review and derived from handbooks or original communications have been recalculated on the basis of these key quantities. The enthalpies of dilution of HF solutions were taken from Johnson et al.[18] and the enthalpies of dilution of HCl solutions were taken from the Tables of Cox et al.[19] The heat capacities of the pure substances (except where stipulated otherwise) were taken from a handbook[7] and the heat capacities of solutions were taken from Parker[20].

In the calculation of the enthalpies of reaction from the equilibrium constants, the thermodynamic functions quoted by Glushko[21] were used. Apart from the above key quantities, in the calculation of the ΔH_f° for certain haloethanes it is also necessary to know the enthalpies of formation of ethylene or its halogeno-derivatives.

The enthalpy of formation of chlorotrifluoroethylene, $\Delta H_f^\circ[C_2F_3Cl(gas)] = -515.1 \pm 3.4$ kJ mol^{-1}, was taken from a recent study[10]; the reasons for its selection are given below (in Section III). The enthalpy of formation of vinyl bromide, $\Delta H_f^\circ[C_2H_3Br(gas)] = 79.3 \pm 1.9$ kJ mol^{-1}, was taken from a handbook[9] where it was recommended on the basis of the enthalpy of hydrogenation of C_2H_3Br to C_2H_6 measured by Lacher et al.[22] The enthalpies of formation of all the remaining haloethylenes were taken from Glushko's handbook[21]. All the recommended values in two handbooks[9,21] were calculated on the basis of the same system of key quantities which was adopted in the present study and their employment does not therefore impair the mutual consistency of the enthalpies of formation. The values $\Delta H_f^\circ[C_2H_4(gas)] = 52.4 \pm 0.5$ kJ mol^{-1} and $\Delta H_f^\circ[C_2F_4(gas)] = -659.5 \pm 2.5$ kJ mol^{-1} have been recommended[21] on the basis of reliable experimental data of several workers. The quantity $\Delta H_f^\circ[C_2H_3Cl(gas)] = 23.0 \pm 2.1$ kJ mol^{-1} was adopted on the basis of measurements of the enthalpy of polymerisation of liquid C_2H_3Cl,[23] the enthalpy of formation of the polymer[24], and the enthalpy of vaporisation of $CH_2 = CHCl$ quoted by Glushko[7]. The quantity $\Delta H_f^\circ[1,1\text{-}C_2H_2Cl_2(gas)] = 2.3 \pm 1.4$ kJ mol^{-1} is based on precise calorimetric measurements of the enthalpy of formation[24,25] and the enthalpy of vaporisation[26].

The enthalpies of formation of *cis*- and *trans*-1,2-$C_2H_2Cl_2$. .(gas) have been found[21] by adjusting the enthalpies of formation of the liquid isomers[27] for consistency with the enthalpies of vaporisation measured in several studies and on the basis of an investigation of the *cis*–*trans* isomerisation equilibrium[28–30]. This led to $\Delta H_f^\circ = 4.1 \pm 1.0$ and 6.1 ± 1.0 kJ mol^{-1} for *cis*- and *trans*-$C_2H_2Cl_2$(gas) respectively. The enthalpies of formation of tri- and tetra-chloroethylenes have been calculated[21] from measurements[27] of their enthalpies of combustion in the liquid state using the enthalpies of vaporisation measured calorimetrically[31]: $\Delta H_f^\circ[C_2HCl_3(gas)] = -4.1 \pm 1.2$ kJ mol^{-1} and $\Delta H_f^\circ[C_2Cl_4(gas)] = -11.0 \pm 2.1$ kJ mol^{-1}. The quantity $\Delta H_f^\circ[1,1\text{-}C_2F_2Cl_2(gas)] = -338 \pm 11$ kJ mol^{-1} has been recommended on the basis of measurements[11] of the enthalpies of hydrogenation of 1,1-$C_2F_2Cl_2$ to 1,1-$C_2H_4F_2$ in the gas phase and the enthalpy of formation of gaseous 1,1-$C_2H_4F_2$ determined by Kolesov et al.[32]

Among the ΔH_f° for haloethylenes indicated, the most reliable are those for C_2H_4, C_2F_4, 1,1-$C_2H_2Cl_2$, and C_2F_3Cl. The majority of other ΔH_f° for haloethylenes have been determined with a relatively low accuracy and their use for the calculation of the ΔH_f° for haloethanes therefore introduces a considerable additional error and is as a rule undesirable.

III. METHODS FOR THE DETERMINATION OF THE ENTHALPIES OF FORMATION OF HALOETHANES

All the experimental methods for the determination of the enthalpies of formation of haloethanes described in the literature can be divided, with very rare exceptions, into two large groups: calorimetric measurements and determination of equilibrium constants. The most important results for this range of substances have been undoubtedly obtained by calorimetric methods, among which the most universal is the method of combustion in a bomb calorimeter. When it is used to determine the ΔH_f° for organohalogen compounds, particularly those with a high halogen content, complications arise due to the low specific energy of combustion of the substances, the complex composition and high corrosion activity of the combustion products, and the occurrence of side reactions. These complications can be partly overcome by employing special apparatus (for example, calorimeters with rotating bombs lined with platinum), auxiliary substances, reductants, careful analysis of the combustion products, etc.; however, all these procedures undoubtedly complicate the method and have an unfavourable effect on the accuracy of the measurements[33,34]. Furthermore, in view of the low specific energy of the combustion of many haloethanes, more stringent requirements must be imposed on the purity of the test specimens.

However, despite these complications, the method of combustion in a bomb has many valuable advantages (in the first place the fact that the apparatus and method have been thoroughly developed and comprehensively tested, the high accuracy of the calorimetric measurements, and the possibility of careful analysis of the combustion products in both gaseous and condensed phases). The fact that the method of determination of the combustion energies in calorimeters with a rotating bomb has been significantly improved in recent years is also important.

In the Laboratory of Thermochemistry at Moscow State University, the method was modernised by increasing the accuracy of the measurement of the temperature and temperature control, by careful study of the processes occurring in the bomb, and partly by employing new more accurate methods of analysis of the combustion products. The changes introduced into the method have already been described[35,36].

The improvements in the method of determination of the energy of combustion in rotating bomb calorimeters made it possible to apply it to the study of new groups of haloethanes: compounds containing different halogen atoms (for example, $CF_3CHClBr$ and $CF_2BrCHFCl$), gaseous and volatile Freons (CF_2ClCF_2Cl and $CF_2ClCFCl_2$), etc.

The determination of the energies of combustion of gaseous haloethanes in a bomb calorimeter involves additional complications, since, as usual, the entire gas does not react and the amount of combusted substance can be determined only from the results of the analysis of the combustion products[37]. The method of combustion of gases in a calorimeter with a burner at a pressure close to atmospheric yields more accurate results[38,39]. However, this method is applicable only to compounds with a low halogen content, mainly to monochloroalkanes[38]. At the present time the majority of enthalpies of combustion of gaseous haloethanes have been obtained by combustion in a bomb.

The method of combustion in the liquefied state in a bomb calorimeter of substances which are gaseous at room temperature, developed recently, is extremely valuable for the

investigation of haloethanes[10,36]. Its principal advantage is almost complete combustion of the test substances. A specially designed crucible container has been used for the liquefaction and combustion of such substances. The method has been developed in a series of calorimetric experiments on the determination of the energies of combustion of chlorotrifluoroethylene[10]. $\Delta H_f^\circ[CF_2 = CFCl(gas)] = -515.1 \pm 3.4$ kJ mol^{-1} has been obtained. Previous determinations of this quantity by measuring the enthalpies of reactions with alkali metals yielded markedly divergent results: -502.3,[40] -549.1,[41] and -565.5 kJ mol^{-1}.[42] The reliability of the determination of $\Delta H_f^\circ[CF_2 = CFCl(gas)]$ obtained in the above study[10] is confirmed by the similarity of the values found by two other procedures: on the basis of the experimental[43] enthalpy of combustion of $CF_2ClCFCl_2$ using the enthalpies of chlorination[44] of chlorotrifluoroethylene, which yielded $\Delta H_f^\circ[CF_2 = CFCl(gas)] = -522.0 \pm 3.4$ kJ mol^{-1}, and also the experimental[45] enthalpy of combustion of $CF_2BrCHFCl$ and the experimental[46] enthalpy of hydrobromination of chlorotrifluoroethylene, which yielded $\Delta H_f^\circ[CF_2 = CFCl(gas)] = -509.5 \pm 5.6$ kJ mol^{-1}. The method developed by Erastov and Kolesov[10] leads to extensive possibilities for the investigation of the thermochemical properties of substances which are not fully combusted in the bomb in the gaseous state.

The results of measurements of the enthalpies of the catalytic halogenation, hydrohalogenation, and hydrogenation of ethylene and its halogeno-derivatives in the gaseous state are frequently used for the calculation of the ΔH_f° of haloethanes. A whole series of such measurements have been carried out by Lacher and co-workers[11,12,22,44,46-50] in a specially designed isothermal calorimeter of the compensation type. In these investigations a fairly high reproducibility of the experimental results was achieved (usually to within ~ 0.5–1.0 kJ mol^{-1}). However, significant systematic discrepancies with data obtained by other methods were also observed in certain cases and it was therefore suggested that the catalyst employed is insufficiently inert[39]. Calculation of ΔH_f° for haloethanes from the data of Lacher and co-workers as a rule requires the knowledge of the ΔH_f° for other organohalogen compounds (for example, haloethylenes).

In order to determine the enthalpies of formation of gaseous chlorofluorocarbons (including chlorofluoroethanes), the method of measurement of the enthalpies of reaction of these compounds with alkali metals has been frequently used[3,40-42]. The reactions are initiated by an electric arc whose energy has to be measured accurately. This method is less accurate than the determination of the heats of combustion owing to the complexity of the composition of the products formed and the need to introduce numerous corrections[3]. The ΔH_f° for haloethanes have been sometimes determined by measuring the enthalpies of reactions which can be achieved only for a few compounds. Thus $\Delta H_f^\circ(C_2F_6)$ has been determined by measuring the enthalpy of the reaction of hexafluoroethane with nitrogen trifluoride[51]. Other cases are examined in Section IV.

Numerous enthalpies of formation of haloethanes have been obtained by measuring the equilibrium constants. The enthalpy of reaction is related to the equilibrium constant by the familiar expression

$$\Delta H_T^0 = -RT \ln K_p + T\Delta S_T^0 \ . \qquad (1)$$

Having measured K_p at several temperatures and having assumed that ΔH_T° and ΔS_T° are constant in the experimental temperature range, it is possible to find the ΔH_T° from the temperature variation of ln K_p (the method of the Second Law of Thermodynamics). If the entropies of the reactants are known, a more accurate calculation of ΔH_T° by the direct substitution of ΔS_T° in Eqn.(1) is possible (the method of the Third Law of Thermodynamics); in principle, it is then sufficient to measure the equilibrium constant at a single temperature. The similarity of the values of ΔH° found on the basis of the Second and Third Laws of Thermodynamics usually indicates the absence of systematic errors from the experimental data. The necessary conditions for the determination of reliable enthalpies of reaction from the study of equilibria are an accurate measurement of the concentrations and (or) pressures of the reactants, careful monitoring of the attainment of the state of equilibrium and, in calculations based on the Second Law, also a fairly wide temperature range of the measurements. In a highly sophisticated experiment, the results of the determination of the enthalpies of reaction by measuring the equilibrium constants are frequently not inferior in their accuracy and reliability to the results of calorimetric measurements.

IV. ANALYSIS OF EXPERIMENTAL DATA AND SELECTION OF THE RECOMMENDED ENTHALPIES OF FORMATION

Ethane

The bibliography of studies on the determination of ΔH_f° for ethane has already been published[7,21]. The most reliable measurements of the enthalpies of combustion of gaseous ethane in a flow calorimeter were carried out by Rossini[52] and Pittam and Pilcher[53]. The amount of combusted ethane was determined by analysing the combustion products for H_2O[52] and CO_2.[53] The values of $\Delta H_f^\circ[C_2H_6(gas)]$ obtained are similar: -84.73 ± 0.48 kJ mol^{-1} [52] and -83.87 ± 0.24 kJ mol^{-1},[55] but the difference between them is nevertheless outside the limits of error. Pittam and Pilcher[53] used a purer specimen than that in Rossini's investigation[52]. However, in the latter study[52] the heat capacity of the calorimeter was determined by measuring the electrical energy, while Pittam and Pilcher found it from the heat of combustion of hydrogen, which renders their results dependent on their latter quantity; it was taken from Rossini's determinations. $\Delta H_f^\circ[C_2H_6.(gas)] = -84.0 \pm 0.4$ kJ mol^{-1} is recommended. It agrees with the value adopted by Glushko[21] as a result of the joint treatment of Rossini's[52] and Pittam and Pilcher's[53] data and the results of studies[54-56] in which the enthalpies of formation and hydrogenation of ethylene were measured.

Hexafluoroethane

The enthalpy of formation of hexafluoroethane has been determined by different methods: by measuring the enthalpy of the reaction of C_2F_6 with potassium[51] or nitrogen trifluoride[51]:

$$C_2F_6\,(gas) + {}^2/_3NF_3\,(gas) \rightarrow 2CF_4\,(gas) + {}^1/_2N_2\,(gas) \qquad (2)$$

and by investigating the equilibria in the reactions[57]

$$C_2F_6\,(gas) + Br_2\,(gas) \rightleftarrows 2CF_3Br\,(gas) \qquad (3)$$

or[58]

$$2CF_3CN\,(gas) \rightleftarrows C_2F_6\,(gas) + C_2N_2\,(gas)\ . \qquad (4)$$

The result obtained by Kirkbride and Davidson[41] is doubtful, since they did not characterise the purity of the substances and did not introduce all the necessary corrections for side reactions. The most reliable value has been obtained[21] by adjusting for mutual consistency the thermochemical data for reactions involving C_2F_6, CF_3Br, CF_3I, CF_3Cl, and CHF_3, including reactions (2)–(4): $\Delta H_f^\circ[C_2F_6(gas)] = -1344.0 \pm 4.0$ kJ mol^{-1}.

1,1-Difluoroethane

The enthalpy of combustion of gaseous CH_3CHF_2 in a bomb calorimeter has been determined[32]: $\Delta H_C^\circ = -1219.6 \pm 8.4$ kJ mol^{-1}. Mass-spectrometric analysis of the combustion products failed to reveal the presence of any fluoro-derivatives, except for a small amount of CH_3CHF_2 which had not reacted. Calculation of the enthalpy of formation using the key quantities adopted above leads to $\Delta H_f^\circ[CH_3CHF_2(gas)] = -497.0 \pm 8.5$ kJ mol^{-1}. Lacher et al.[11] measured ΔH° for the hydrogenation of $CF_2 = CCl_2$ with formation of CH_3CHF_2. However, these data were not used to calculate $\Delta H_f^\circ(CF_2 = CCl_2)$ (see Section II).

1,1,1-Trifluoroethane

The enthalpy of combustion of gaseous 1,1,1-trifluoroethane has been measured[59]: $\Delta H_C^\circ[CH_3CF_3(gas)] = -1008.3 \pm 1.7$ kJ mol^{-1}. A correction for adjustment to the standard state was not applied[59]; we calculated it on the basis of the calorimetric experimental data presented in the above study[59] and found it to be 4 ± 2 kJ mol^{-1}. When account is taken of this correction, we obtain $\Delta H_f^\circ[CH_3CF_3(gas)] = -748.7 \pm 3.2$ kJ mol^{-1}. A very similar value was obtained[60] by calculation from the dissociation energy of the C–C bond in 1,1,1-trifluoroethane found from kinetic data for the dehydrofluorination of CH_3CF_3: $\Delta H_f^\circ[CH_3CF_3(gas)] = -747.3$ kJ mol^{-1}. This method is much less accurate than that employed by Kolesov and Martynov[59].

1,1,2-Trifluoroethane

Lacher et al.[11] measured the enthalpy of hydrogenation of chlorotrifluoroethylene at 401 K:

$$CF_2 = CFCl\,(gas) + 2H_2\,(gas) \rightarrow CH_2FCHF_2\,(gas) + HCl\,(gas). \qquad (5)$$

They found $\Delta H_{401}^\circ(5) = -271.6$ kJ. After adjustment to the standard temperature, we obtain $\Delta H_{298}^\circ(5) = -268.2$ kJ, whence $\Delta H_f^\circ[CH_2FCHF_2(gas)] = -691 \pm 10$ kJ mol^{-1}. The error was estimated approximately in view of the lack of the necessary information in the above study[11] for its calculation.

Hexachloroethane

Berthelot[61] determined the enthalpy of combustion of hexachloroethane by an obsolete method which did not ensure the complete reduction of chlorine. Smith et al.[27] used the "quartz spiral" method and showed that it makes it possible to measure the heats of combustion of organochlorine compounds with an accuracy close to that of measurements in a rotating bomb calorimeter. They recalculated the results obtained previously by this method after introducing a series of necessary corrections. However, an important disadvantage of the study of Smith et al.,[27] which lowers the reliability of the determinations, is the absence of data on the purities of the test substances. Furthermore, the influence of impurities on the measurements of ΔH_C° is particularly marked for compounds with a high chlorine content. The data of Smith et al.[27]† for hexachloroethane yield $\Delta H_f^\circ[C_2Cl_6(cryst.,$ orthorhomb.$)] = -198.4 \pm 2$ kJ mol^{-1}. Taking into account the enthalpy of sublimation ($\Delta H_{s,298}^\circ = 60.7 \pm 4.2$ kJ mol^{-1}[7,21]), we find $\Delta H_f^\circ[C_2Cl_6(gas)] = -137.7 \pm 4.7$ kJ mol^{-1}. The accuracy of the enthalpy of sublimation of hexachloroethane is likewise low. The value of $\Delta H_{s,298}^\circ$ was calculated by Glushko[7,21] as the sum of three experimental quantities: the enthalpy of vaporisation of C_2Cl_6(cryst.,triclin.) and the enthalpies of fusion of the triclinic and orthorhombic modifications. Thus the value of $\Delta H_f^\circ[C_2Cl_6(gas)]$ found from the data of Smith et al.[27] cannot be regarded as sufficiently reliable.

Kirkbride[63] measured the enthalpy of chlorination of liquid tetrachloroethylene and the enthalpy of solution of C_2Cl_6 in C_2Cl_4, whence he found $\Delta H_{298}^\circ(6) = -155.2$ kJ for the reaction

$$C_2Cl_4\,(liq.) + Cl_2\,(gas) = C_2Cl_6\,(cryst.). \qquad (6)$$

$\Delta H_f^\circ[C_2Cl_6(gas)] = -145.2$ kJ mol^{-1} corresponds to the value. Kirkbride's study[63] was not precise; the slowness of the chlorination reaction made it necessary to introduce several large corrections which were not determined with adequate accuracy. His result must therefore be regarded as merely approximate.

The equilibrium in the gas-phase catalytic reaction

$$C_2Cl_4\,(gas) + Cl_2\,(gas) \rightleftarrows C_2Cl_6\,(gas). \qquad (7)$$

has been investigated[64–67]. We calculated $\Delta H_{298}^\circ(7) = -127.0$ kJ in accordance with the Third Law of Thermodynamics from the equilibrium constant measured[64,65] at 776 K, whence $\Delta H_f^\circ[C_2Cl_6(gas)] = -138.0$ kJ mol^{-1}. The equilibrium constants were measured[66,67] at three temperatures in the range 773–873 K and the enthalpy of reaction (7) has been found from the temperature variation of K_p: $\Delta H_{853}^\circ(7) = -130.5$ kJ. Adjustment to the standard temperature leads to $\Delta H_{298}^\circ(7) = -136.9$ kJ. Calculation of the enthalpy of reaction (7) in accordance with the Third Law of Thermodynamics yields three similar values: −139.7, −140.0, and −140.1 kJ. Using the average $\Delta H_{298}^\circ(7) = -139.9$ kJ, we obtain $\Delta H_f^\circ[C_2Cl_6(gas)] = -150.9$ kJ mol^{-1}. The results of the calculation of $\Delta H_{298}(7)$ by two methods from the data of Bushneva and co-workers[66,67] agree satisfactorily. However, in the calculation of $\Delta H_f^\circ(C_2Cl_6)$ it is necessary to employ the value of $\Delta H_f^\circ(C_2Cl_4)$ determined by Smith et al.,[27] the deficiencies of whose work were mentioned above.

Thus it is difficult to recommend a reliable value of $\Delta H_f^\circ[C_2Cl_6(gas)]$ on the basis of the available experimental data. Its calculated value is presented below (Section VI).

Chloroethane

Several workers[39,68–70] determined ΔH_C° for gaseous chloroethane in a calorimeter with a burner. Studies of Berthelot[68] and Thomsen[69] are only of historical interest. The precision of the method used by Casey and Fordham[70] was not high: the calorimeter was calibrated against the heat of combustion of a known volume of hydrogen; there is a large fraction of ballast heat due to the combustion of hydrogen in the mixture with chloroethane; quantitative characteristics of the purity of the reactants are not given. Casey and Fordham[70] obtained $\Delta H_f^\circ[C_2H_5Cl(gas)] = -100 \pm 10$ kJ mol^{-1}. The most reliable data are those of Fletcher and Pilcher[39] who used pure specimens and carried out a careful analysis of the combustion products. They obtained $\Delta H_C^\circ[C_2H_5Cl(gas)] = -1413.05 \pm 0.59$ kJ mol^{-1}, which corresponds to $\Delta H_f^\circ[C_2H_5Cl.(gas)] = 112.2 \pm 0.7$ kJ mol^{-1}.

Similar results were obtained from the results of a study of the equilibrium reaction

$$C_2H_4\,(gas) + HCl\,(gas) \rightleftarrows C_2H_5Cl\,(gas) \qquad (8)$$

† All the values of ΔH_C° for chloroethanes quoted by Smith et al.[27] were measured at 292 K; in the present review they have been adjusted to the standard temperature. The heat capacity of C_2Cl_6 was taken from Rossini et al.[62] and those of all the remaining substances were taken from Glushko's handbook[7].

by Lane et al.[71] (at 722–754 K) and Howlett[72] (at 448–528 K). Lane et al.[71] obtained $\Delta H^\circ_{743}(8) = 74.98$ kJ on the basis of the Third Law of Thermodynamics and Howlett[72] obtained $\Delta H^\circ_{463}(8) = -72.97$ kJ on the basis of the Second Law of Thermodynamics. Hence, after adjustment to 298 K, we obtain $\Delta H^\circ_f[C_2H_5Cl(gas)] = -110.8 \pm 2$ and -111.1 ± 2 kJ mol^{-1} respectively. An earlier and less accurate study[73] of equilibrium (8) yielded $\Delta H^\circ_f[C_2H_5Cl(gas)] = -96.0$ kJ mol^{-1}. Measurements of Lacher and co-workers[7,48] of the enthalpy of hydrogenation of chloroethane at 521 K ($\Delta H_r = -71.80$ kJ mol^{-1}) lead to $\Delta H^\circ_f[C_2H_5Cl(gas)] = 106.7$ kJ mol^{-1} after adjustment to the standard temperature. The value obtained by Fletcher and Pilcher[39] is recommended: $\Delta H^\circ_f[C_2H_5Cl.(gas)] = -112.2 \pm 0.7$ kJ mol^{-1}.

1,1-Dichloroethane

Thomsen's study[69] involving the measurement of the enthalpy of combustion of CH_3CHCl_2 is merely of historical interest. Later measurements of ΔH°_C yielded $\Delta H^\circ_f[CH_3CHCl_2.(liq.)] = 158.3 \pm 0.9$ kJ mol^{-1} or (when account is taken of the enthalpy of evaporation $\Delta H^\circ_{v,298} = 31.00 \pm 0.04$ kJ mol^{-1} [7]), $\Delta H^\circ_f[CH_3CHCl_2(gas)] = -127.3 \pm 0.9$ kJ mol^{-1} were obtained[27]. Lacher et al.[50] determined ΔH for reaction

$$CH_3CHCl_2\,(gas) + 2H_2\,(gas) \rightarrow C_2H_6\,(gas) + 2HCl\,(gas) \qquad (9)$$

at 523 K. Their data yield $\Delta H^\circ_{298}(9) = -139.9 \pm 2.5$ kJ and $\Delta H^\circ_f[CH_3CHCl_2(gas)] = -128.8 \pm 2.6$ kJ mol^{-1}. The results of Smith et al.[27] and Lacher et al.[50] are similar and yet it is difficult to regard them as reliable. Thus the sign of ΔH for the isomerisation of dichloroethane which follows from the values of $\Delta H^\circ_f[C_2H_4Cl_2(gas)]$ found in the above studies[27,50] conflicts with that determined directly[74] (see below). The purity of the CH_3CHCl_2 specimen used by Lacher et al.[50] was low (99% according to chromatographic analysis); the method used to check that the reaction proceeds unambiguously is not indicated. Smith et al.[27] totally fail to give any information about the purity of the specimen.

More reliable data were obtained by Levanova et al.[75] in the study of the equilibria

$$CH_3CHCl_2\,(gas) \rightleftarrows CH_2{=}CHCl\,(gas) + HCl\,(gas) \qquad (10)$$

and

$$CH_2{=}CHCl\,(gas) + HCl\,(gas) \rightleftarrows CH_3CHCl_2\,(liq.) \qquad (11)$$

in the temperature ranges 403–438 K and 293–323 K respectively. They calculated $\Delta H^\circ_{420}(10) = 61.7$ kJ and $\Delta H^\circ_{308}(11) = -92.7$ kJ on the basis of the Second Law of Thermodynamics; $\Delta S^\circ_{420}(10) = 144.3$ kJ mol^{-1} K^{-1} and $\Delta S^\circ_{308}(11) = -238.9$ J mol^{-1} K^{-1}. Adjustment to the standard temperature yields $\Delta H^\circ_{298}(10) = 60.9$ kJ, whence follows $\Delta H^\circ_f[CH_3CHCl_2(gas)] = -130.2$ kJ mol^{-1}; $\Delta H^\circ_f[CH_3CHCl_2(gas)] = -131.0$ kJ mol^{-1} corresponds to $\Delta H^\circ_{298}(11)$. The similarity of the ΔH°_f found from the ΔH for reactions (10) and (11) indicates the absence of significant systematic errors.

Another confirmation of the validity of the results of Levanova et al.[75] is the satisfactory agreement between the experimental $\Delta S^\circ(10)$ and $\Delta S^\circ(11)$ and those calculated from the data in Glushko's handbook[7]: $\Delta S^\circ_{420}(10) = 148.4$ J mol^{-1} K^{-1} and $\Delta S^\circ_{298}(11) = -239.0$ J mol^{-1} K^{-1}. The average of the two values of ΔH°_f found by Levanova et al.[75] is recommended, i.e. $\Delta H^\circ_f[CH_3CHCl_2(gas)] = -130.6 \pm 3.0$ kJ mol^{-1}. The error was estimated by analogy with the results of the study of equilibria in other investigations by the same workers.

1,2-Dichloroethane

The values of ΔH°_C for 1,2-dichloroethane have been determined[69,76] but their accuracy is low. The enthalpies of combustion of liquid CH_2ClCH_2Cl found by Smith et al.[27] lead to $\Delta H^\circ_f[CH_2ClCH_2Cl(liq.)] = -158.9 \pm 0.8$ kJ mol^{-1}. When account is taken of the enthalpy of evaporation $\Delta H^\circ_{v,298} = 35.4 \pm 0.4$ kJ mol^{-1},[7] we obtain $\Delta H^\circ_f[CH_3CHCl_2(gas)] = 123.5 \pm 0.9$ kJ mol^{-1}. Later determinations[24,77] of $\Delta H^\circ_C(CH_2ClCH_2Cl)$ lead to $\Delta H^\circ_f[CH_2ClCH_2Cl(gas)] = -129.5 \pm 1.6$ and -134.1 ± 1.2 kJ mol^{-1} respectively.

The enthalpy of the reaction

$$CH_2ClCH_2Cl\,(gas) + 2H_2\,(gas) \rightarrow C_2H_6\,(gas) + 2HCl\,(gas) \qquad (12)$$

found by Lacher et al.[50] at 523 K leads to $\Delta H^\circ_{298}(12) = -142.1 \pm 2.5$ kJ and $\Delta H^\circ_f[CH_2ClCH_2Cl(gas)] = -126.6 \pm 2.6$ kJ mol^{-1} after adjustment to the standard temperature. As in the hydrogenation of 1,1-dichloroethane (see above), the specimen employed by Lacher et al.[50] was not highly pure (99%) and the absence of side reactions was not confirmed.

Conn et al.[78] determined ΔH° for the chlorination of ethylene in the gas phase at 355 K: $\Delta H^\circ_r = -182.6 \pm 0.6$ kJ mol^{-1}. After adjustment to 298 K, their data lead to $\Delta H^\circ_f[CH_2ClCH_2.Cl(gas)] = -130.4 \pm 0.8$ kJ mol^{-1}. The studies of Sinke and Stull[24], Hu and Sinke[77], and Conn et al.[78] were carried out by well tested methods using fairly pure specimens. However, one must note that the results of Hu and Sinke[24] and Conn et al.,[78] like those of Smith et al.[27] and Lacher et al.,[50] conflict with the determination[74] of ΔH for the isomerisation reaction

$$CH_3CHCl_2 \rightleftarrows CH_2ClCH_2Cl \qquad (13)$$

[$\Delta H^\circ_{385}(13) = -9.6 \pm 1.4$ kJ was obtained]. The latter value was found by the joint treatment of the results of measurements of K_p in the liquid and gas phases and is only approximate. Nevertheless its sign and approximate value must be taken into account in selecting the ΔH°_f for 1,2-dichloroethane. On the basis of these considerations, preference must be given to the data of Hu and Sinke[77], who determined ΔH°_C by the most reliable method—in a rotating bomb calorimeter, and $\Delta H^\circ_f[CH_2ClCH_2Cl(gas)] = -134.1 \pm 1.2$ kJ mol^{-1} must be adopted.

1,1,1-Trichloroethane

The enthalpy of combustion of 1,1,1-trichloroethane in rotating bomb calorimeters has been measured by a number of workers[25,77,79]. It has been shown[79] that the result obtained previously, namely $\Delta H^\circ_f[CH_3CCl_3(gas)] = -138.3$ kJ mol^{-1},[77] was erroneous owing to the inadequate purity of the specimen. In two investigations[25,79] the purities of the specimens were extremely high (99.99 and 99.96 mole % respectively). Both studies were carried out using a thoroughly tested method. The values of ΔH°_C from the above investigations[25,79] together with $\Delta H^\circ_{v,298}(CH_3CCl_3) = 32.47 \pm 0.07$[80] yield $\Delta H^\circ_f[CH_3CCl_3(gas)] = -142.1 \pm 1.4$ kJ mol^{-1}[25] and -146.1 ± 1.1 kJ mol^{-1}.[79] Hu et al.[79] also investigated the equilibrium

$$CH_2{=}CCl_2\,(gas) + HCl\,(gas) \rightleftarrows CH_3CCl_3\,(gas) \qquad (14)$$

at 348–399 K and obtained $\Delta H^\circ_{298}(14) = -54.6 \pm 8$ kJ on the basis of the Third Law of Thermodynamics. Hence we find $\Delta H^\circ_f[CH_3CCl_3(gas)] = -144.6 \pm 1.7$ kJ mol^{-1}.

The equilibrium in the hydrochlorination of 1,1-dichloroethylene in chlorobenzene at 293–353 K has been studied by Levanova et al.[81] They found $\Delta H^\circ_{323} = -56.9 \pm 2$ kJ mol^{-1}, from which follows $\Delta H^\circ_f[CH_3CCl_3(gas)] = -141.0 \pm 2.4$ kJ

mol^{-1}, its accuracy being lower than that of the results of other investigations[25,79], since no account has been taken of the enthalpy of solution of $CH_2=CCl_2$ and CH_3CCl_3 in chlorobenzene.

The weighted average of the most reliable results[25,79] presented above is recommended: $\Delta H_f^\circ[CH_3CCl_3(gas)] = -144.6 \pm 0.8$ kJ mol^{-1}.

1,1,2-Trichloroethane

Kirkbride[63] measured the enthalpy of the reaction

$$CH_2ClCH_2Cl\ (liq.) + Cl_2\ (gas) \rightarrow CH_2ClCHCl_2\ (liq.) + HCl\ (gas) \qquad (15)$$

and found $\Delta H_{298}^\circ(15) = -116.3$ kJ. Using the value of $\Delta H_f^\circ(CH_2ClCH_2Cl)$ adopted above, we obtain $\Delta H_f^\circ[CH_2ClCHCl_2.(liq.)] = -193.5$ kJ mol^{-1}. Kirkbride[63] introduced fairly large corrections for the dissolution of HCl, the evaporation of dichloroethane, etc., which had not been measured with adequate accuracy; no check was made to make sure that side reactions do not occur. His result must therefore be regarded as only approximate.

Levanova et al.[82] investigated the equilibria in the hydrochlorination of *cis*- and *trans*-dichloroethylenes in solution in tetrachloroethane. Without taking into account the heats of solution, we obtain from these results $\Delta H_f^\circ[CH_2ClCHCl_2.(liq.)] = -179.9$ and -181.9 kJ mol^{-1}. The result based on the study of the equilibrium in the isomerisation reaction

$$CH_2ClCHCl_2\ (liq.) \rightleftarrows CH_3CCl_3\ (liq.) \qquad (16)$$

at 373–473 K is more reliable[82]. Calculation based on the Second Law of Thermodynamics yielded $\Delta H_{423}^\circ(16) = 8.4 \pm 1.7$ kJ. Hence, having adopted $\Delta C_p(liq.) = \Delta C_p(gas) = 3.8$ J mol^{-1} K^{-1} [17]# in view of the lack of data for $C_p[CH_2.ClCHCl_2(liq.)]$, we find $\Delta H_{298}^\circ(16) = 7.9 \pm 1.7$ kJ and $\Delta H_f^\circ.[CH_2ClCHCl_2(liq.)] = -185.0 \pm 1.9$ kJ mol^{-1}. Taking into account the enthalpy of evaporation $\Delta H_{v,298}^\circ = 40.28 \pm 0.06$ kJ mol^{-1},[80] we have $\Delta H_f^\circ[CH_2ClCHCl_2(gas)] = -144.7 \pm 1.9$ kJ mol^{-1}.

1,1,1,2-Tetrachloroethane

The enthalpy of combustion of liquid CH_2ClCCl_3 (purity 99.95 mole %) has been measured[83] in a tantalum rotating bomb calorimeter and $\Delta H_c^\circ[CH_2ClCCl_3(liq.)] = -973.90 \pm 1.28$ kJ mol^{-1} was obtained. This leads to $\Delta H_f^\circ[CH_2ClCCl_3(liq.)] = -193.45 \pm 1.35$ kJ mol^{-1}; taking into account $\Delta H_{v,298}^\circ = 41.1 \pm 0.2$ kJ mol^{-1},[83] we find that $\Delta H_f^\circ[CH_2ClClCCl_3(gas)] = 152.3 \pm 1.4$ kJ mol^{-1}.

Levanova et al.[84] found $\Delta H_{333}^\circ = 45.4 \pm 0.4$ kJ mol^{-1} from the temperature variation of the equilibrium constants for the dehydrochlorination of 1,1,1,2-tetrachloroethane. Hence we obtain $\Delta H_{r,298}^\circ = 44.0 \pm 0.4$ kJ mol^{-1} and $\Delta H_f^\circ[CH_2ClCCl_3.(gas)] = -133.3$ kJ mol^{-1}. This result is less accurate than the data of Gundry and Head[83].

1,1,2,2-Tetrachloroethane

Smith et al.[27] determined the enthalpy of combustion of 1,1,2,2-tetrachloroethane: $\Delta H_c^\circ = -970.0 \pm 1.4$ kJ mol^{-1}. From this data, we obtain $\Delta H_f^\circ[CHCl_2CHCl_2(liq.)] = 193.0 \pm 1.5$ kJ mol^{-1} or (taking into account the enthalpy of evaporation $\Delta H_{v,298}^\circ = 45.78 \pm 0.16$ kJ mol^{-1} [80]) $\Delta H_f^\circ[CHCl_2CHCl_2.(gas)] = -147.2 \pm 1.5$ kJ mol^{-1}. The ΔH° for the chlorination of *cis*-dichloroethylene measured by Kirkbride[63] leads to a similar value: $\Delta H_f^\circ[CHCl_2CHCl_2(gas)] = -148.2$ kJ mol^{-1}. More reliable results were obtained in a study[67] where the equilibrium constants of the isomerisation reaction

$$CHCl_2CHCl_2\ (liq.) \rightleftarrows CH_2ClCCl_3\ (liq.) \qquad (17)$$

were measured at three temperatures in the range 453–493 K and the enthalpy of reaction (17) was calculated on the basis of the Second Law of Thermodynamics; $\Delta H_{473}^\circ(17) = 10.0 \pm 2.6$ kJ was obtained. Having adopted $\Delta C_p(liq.) = \Delta C_p(gas) = 2.1$ J mol^{-1} K^{-1} [7] for adjustment to 298 K (in view of the lack of the heat capacity of liquid CH_2ClCCl_3), we obtain $\Delta H_{298}^\circ(17) = 9.7 \pm 2.6$ kJ. Together with the value of $\Delta H_f^\circ.[CH_2ClCl_3(liq.)]$ quoted above, this yields $\Delta H_f^\circ[CHCl_2CHCl_2.(liq.)] = -203.1 \pm 3.0$ kJ mol^{-1} or $\Delta H_f^\circ[CHCl_2CHCl_2(gas)] = -157.3 \pm 3.0$ kJ mol^{-1}.

Pentachloroethane

The enthalpy of combustion of pentachloroethane measured by Smith et al.,[27] namely $\Delta H_c^\circ = -858.9 \pm 2.5$ kJ mol^{-1}, leads to $\Delta H_f^\circ[C_2HCl_5(liq.)] = -183.5 \pm 2.6$ kJ mol^{-1}. The enthalpy of chlorination of trichloroethylene $\Delta H_r = -150.6$ kJ mol^{-1} obtained by Kirkbride[63] leads to $\Delta H_f^\circ[C_2HCl_5(liq.)] = -188.7$ kJ mol^{-1}.

Bushneva[67] and Levanova et al.[85] determined the equilibrium constants of the catalytic reaction

$$C_2HCl_5\ (soln) \rightleftarrows HCl\ (gas) + C_2Cl_4\ (soln) \qquad (18)$$

at 363–383 K and found $\Delta H_{373}^\circ(18) = 45.1 \pm 4.5$ kJ on the basis of the Second Law of Thermodynamics. Adjustment to the standard temperature yields $\Delta H_{298}^\circ(18) = 48.1 \pm 4.5$ kJ, whence $\Delta H_f^\circ[C_2HCl_5(liq.)] = -191.4 \pm 5$ kJ mol^{-1}.

The deficiencies of the studies of Smith et al.[27] and Kirkbride[63] were already noted above [see the discussion of the value of $\Delta H_f^\circ(C_2Cl_6)$]. The accuracy of the determination of $\Delta H_f^\circ[C_2HCl_5(liq.)]$ in the above investigations[67,85] is also low as a consequence of the narrow temperature range in the measurements of K_p, the lack of enthalpies of solution for C_2Cl_4 and C_2HCl_5, and the use of an insufficiently reliable value of $\Delta H_f^\circ[C_2Cl_4(gas)]$, determined from the data of Smith et al. (see Section II).

The ΔH_f° for gaseous pentachloroethane were found to be -137.9 kJ mol^{-1},[27] -143.1 kJ mol^{-1},[63] and -145.8 kJ mol^{-1}.[67,85] Their reliability is reduced also as a consequence of the use of $\Delta H_{v,298}^\circ(C_2HCl_5) = 45.6$ kJ mol^{-1}, quoted by Kirkbride without indicating the error and the method of measurement. The calculated $\Delta H_f^\circ[C_2HCl_5(gas)]$ is therefore recommended below (see Section VI).

1,2-Dichlorotetrafluoroethane

The values of $\Delta H_f^\circ[CF_2ClCF_2Cl(gas)]$ calculated from the ΔH° for the reactions of CF_2ClCF_2Cl with potassium[41] or sodium[86] are -920.8 and -968.5 kJ mol^{-1} respectively. This discrepancy is probably due to complications arising in the determination of ΔH for reactions with alkali metals.

The measurements of the enthalpy of chlorination of tetrafluoroethylene by Lacher et al.[47] lead to $\Delta H_f^\circ[CF_2ClCF_2Cl.(gas)] = -899.4$ kJ mol^{-1}. The recommended value is based on the enthalpy of combustion of gaseous 1,2-dichlorotetrafluoroethane measured in a rotating bomb calorimeter[87]. The purity of the specimen was 99.8 mole %; a correction was

$\Delta C_p(liq.)$ and $\Delta C_p(gas)$ for dichloroethane isomers do not differ within the limits of experimental errors[7].

applied for the 0.2 mole % C_2F_5Cl impurity. $\Delta H_c^\circ[CF_2ClCF_2Cl.(gas)] = -624.7 \pm 3.6$ kJ mol^{-1} was obtained, whence follows $\Delta H_f^\circ[CF_2ClCF_2Cl(gas)] = -925.5 \pm 4.3$ kJ mol^{-1}.

1,1,2-Trichlorotrifluoroethane

The enthalpy of combustion of $CF_2ClCFCl_2$ was determined by Erastov et al.[43] The measurements were performed in two rotating bomb calorimeters, three specimens with purities of 99.60, 99.85, and 99.91 mole % were used, and the combustion products were carefully analysed. $\Delta H_f^\circ[CF_2Cl.CFCl_2(liq.)] = -755.0 \pm 2.8$ kJ mol^{-1} corresponds to the $\Delta H_c^\circ[CF_2ClCFCl_2(liq.)] = -641.6 \pm 1.9$ kJ mol^{-1} measured[43]. When account is taken of the enthalpy of evaporation $\Delta H_{v,298}^\circ = 28.2 \pm 0.4$ kJ mol^{-1},[88] we find $\Delta H_f^\circ[CF_2ClCFCl_2(gas)] = -726.8 \pm 2.8$ kJ mol^{-1}. When the enthalpy of formation $\Delta H_f^\circ.[CF_2=CFCl(gas)]$ quoted above is used, the result of Erastov et al.[43] agree satisfactorily with the enthalpy of chlorination of chlorotrifluoroethylene obtained by Lacher et al.[44]

The quantity $\Delta H_f^\circ[CF_2ClCFCl_2(gas)] = -781.9$ kJ mol^{-1}, calculated from the measurements of ΔH° for the reaction of $CF_2ClCFCl_2$ with sodium[86], is less reliable.

Tetrachloro-1,1-difluoroethane

The enthalpy of chlorination of 1,1-dichlorodifluoroethylene $\Delta H_{363} = -171.9$ kJ mol^{-1}, to which corresponds $\Delta H_f^\circ[CF_2Cl.CCl_3(gas)] = 510$ kJ mol^{-1}, has been measured[44]. It is noteworthy that the value of $\Delta H_f^\circ[CF_2=CCl_2(gas)] = -338 \pm 11$ kJ mol^{-1} (see Section II) employed in this calculation is not very reliable. The value of ΔH° obtained[44] for the chlorination reaction also gives rise to some doubts, since it deviates from the general relations for the ΔH° for the chlorination of fluoro- and chloro-ethylenes[89].

The value based on the measurement of the enthalpy of combustion of tetrachloro-1,1-difluoroethane (purity 99.6 mole %) in a rotating bomb calorimeter is more reliable[90]; it amounts to $\Delta H_c^\circ[CF_2ClCCl_2(cryst.)] = -670.5 \pm 3.5$ kJ mol^{-1}, whence follows $\Delta H_f^\circ[CF_2ClCCl_3(cryst.)] = -569.8 \pm 3.8$ kJ mol^{-1}. When account is taken of the enthalpy of fusion ($\Delta H_{m,298}^\circ = 3.3 \pm 0.4$ kJ mol^{-1} [90]) and the enthalpy of evaporation ($\Delta H_{v,298}^\circ = 40.7 \pm 1.9$ kJ mol^{-1}) of tetrachloro-1,1-difluoroethane, we obtain $\Delta H_f^\circ[CF_2ClCCl_3(gas)] = -525.8 \pm 4.3$ kJ mol^{-1}.

1-Chloro-1-fluoroethane

The enthalpy of combustion of two specimens of gaseous CH_3CHFCl (with purities of 99.78 and 99.93 mole %) were measured[91] in a rotating bomb calorimeter. $\Delta H_f^\circ[CH_3CHFCl.(gas)] = -313.4 \pm 2.6$ kJ mol^{-1} corresponds to the $\Delta H_c^\circ = -1247.75 \pm 2.5$ kJ mol^{-1} obtained.

1-Chloro-1,1-difluoroethane

The enthalpy of combustion of gaseous CH_3CF_2Cl (99.90 mole % pure) has been measured[92] in a rotating bomb calorimeter: $\Delta H_c^\circ = -1061.1 \pm 5.0$ kJ mol^{-1}. Hence follows $\Delta H_f^\circ.[CH_3CF_2Cl(gas)] = -536.2 \pm 5.2$ kJ mol^{-1}.

Bromoethane

The early determinations[68,69] of ΔH° for the combustion of bromoethane are of only historical interest. Lane et al.[71] investigated the equilibrium in the hydrobromination of ethylene at 515–573 K and calculated $\Delta H_{r,544}^\circ = -80.3 \pm 1.3$ kJ mol^{-1} on the basis of the Second Law of Thermodynamics. After adjustment to the standard temperature, we obtain $\Delta H_{r,298}^\circ = -78.2 \pm 1.3$ kJ mol^{-1} and $\Delta H_f^\circ[C_2H_5Br(gas)] = -62.2 \pm 1.4$ kJ mol^{-1}. The enthalpy of hydrogenation of bromoethane has been measured[49] at 523 K; it amounts to $\Delta H_r^\circ = -62.05 \pm 1.1$ kJ mol^{-1}, whence $\Delta H_{r,298} = -59.51 \pm 1.1$ kJ mol^{-1}. Using the value of $\Delta H_f^\circ[C_2H_6(gas)]$ recommended above, we obtain $\Delta H_f^\circ[C_2H_5Br(gas)] = -60.9 \pm 1.2$ kJ mol^{-1}. The values of ΔH_f° derived from the investigations of Fowell et al.[49] and Lane et al.[71] agree satisfactorily; their weighted mean, i.e. $\Delta H_f^\circ[C_2H_5Br(gas)] = -61.5 \pm 1.0$ kJ mol^{-1}, can be adopted as the most probable.

Ashcroft et al.[93] determined ΔH° for the reaction of C_2H_5Br with lithium hydride and found that the heat of the reaction

$$C_2H_5Br\,(liq.) + {}^1/_2H_2\,(gas) \rightarrow C_2H_6\,(gas) + {}^1/_2Br_2\,(liq.) \qquad (19)$$

is $\Delta H_{328}^\circ(19) = 11.7 \pm 6.3$ kJ. Hence follows $\Delta H_f^\circ[C_2H_5Br.(liq.)] = -95.7 \pm 6.3$ kJ mol^{-1}; bearing in mind that $\Delta H_{v,298}^\circ = 27.91 \pm 0.21$ kJ mol^{-1},[7] we obtain $\Delta H_f^\circ[C_2H_5Br(gas)] = -67.8 \pm 6.3$ kJ mol^{-1}. This value does not conflict with that recommended above but is less accurate.

1,1- and 1,2-Dibromoethanes

Berthelot's data[94] for the enthalpy of bromination of ethylene and also those of Kablukov and Perel'man[76] for the enthalpy of combustion of 1,2-dibromoethane in a static bomb calorimeter are now obsolete.

Measurements of the enthalpy of combustion of liquid CH_2BrCH_2Br in rocking[95] and rotating[96] bomb calorimeters lead to $\Delta H_f^\circ[CH_2BrCH_2Br(gas)] = -52.3$ and -22.4 kJ mol^{-1} respectively when account is taken of $\Delta H_{v,298}^\circ(CH_2BrCH_2Br) = 41.8 \pm 0.4$ kJ mol^{-1}.[7] The large discrepancy between them may be explained by the presence of impurities in the test specimens whose purities were not characterised in the above investigations[95,96].

Conn et al.[78] determined the enthalpy of bromination of ethylene (with a purity of 99.98 mole %) in the gas phase at 355 K; it proved to be -121.6 ± 1.3 kJ mol^{-1}. After adjustment to 298 K, we obtain $\Delta H_{r,298}^\circ = 121.9 \pm 1.3$ kJ mol^{-1}, whence follows $\Delta H_f^\circ[CH_2BrCH_2Br(gas)] = -38.6 \pm 1.4$ kJ mol^{-1}.

Levanova et al.[97] measured the equilibrium constants of the reactions

$$CH_3CHBr_2\,(gas) \rightleftarrows CH_2=CHBr\,(gas) + HBr\,(gas), \qquad (20)$$

$$CH_2BrCH_2Br\,(gas) \rightleftarrows CH_2=CHBr\,(gas) + HBr\,(gas), \qquad (21)$$

$$CH_3CHBr_2\,(gas) \rightleftarrows CH_2BrCH_2Br\,(gas) \qquad (22)$$

at temperatures in the range 404–520 K and calculated the following values on the basis of the Second Law of Thermodynamics: $\Delta H_{425}^\circ(20) = 70.3 \pm 2.5$ kJ, $\Delta H_{448}^\circ(21) = 79.9 \pm 1.7$ kJ, and $\Delta H_{485}^\circ(22) = -12.1 \pm 1.3$ kJ. Adopting $\Delta C_p = 0$ in reactions (20)–(22) owing to the lack of data for $C_p(CH_3.CHBr_2)$ and also in view of the low value of $\Delta C_p(21) = 0.1$ J mol^{-1} K^{-1},[7] we obtain $\Delta H_f^\circ[CH_3CHBr_2(gas)] = -27.4 \pm 3.2$ kJ mol^{-1} and $\Delta H_f^\circ[CH_2BrCH_2Br(gas)] = -37.0 \pm 6$ kJ mol^{-1} from the ΔH° for reactions (20) and (21).

Izmailov et al.[98] investigated the equilibrium in the isomerisation of dibromoethane in the liquid phase at 363–698 K and calculated the enthalpy of isomerisation as 528 K on the basis

of the Second Law of Thermodynamics, which proved to be -13.0 ± 0.5 kJ mol^{-1}. Adopting $\Delta C_p = 0$ and using the value of $\Delta H^\circ_{v,298}(CH_2BrCH_2Br)$[7] quoted above as well as the value $\Delta H^\circ_{v,298}(CH_3CHBr_2) = 39.3$ kJ mol^{-1} calculated by the Klages equation[99], we obtain $\Delta H^\circ_{298}(22) = -10.5 \pm 5.0$ kJ for the gas phase. The error takes into account the approximate nature of the calculation. The results of the determination of the enthalpies of formation of 1,1- and 1,2-dibromoethanes as well as the enthalpies of their isomerisation found in a number of studies[78,97,98] agree with one another (within the limits of the errors). Joint least squares treatment of the five results indicated, taking into account their statistical weights, yielded the following recommended values: $\Delta H^\circ_f[CH_3CHBr_2.(gas)] = -26.7 \pm 1.9$ kJ mol^{-1} and $\Delta H^\circ_f[CH_2BrCH_2Br(gas)] = -38.3 \pm 1.2$ kJ mol^{-1}.

1,2-Dibromotetrafluoroethane

Lacher et al.[12] measured the enthalpy of bromination of gaseous tetrafluoroethylene at 376 K and found it to be -161.0 ± 3.0 kJ mol^{-1}. Using $C_p[CF_2BrCF_2Br(gas)] = 119.8$ J mol^{-1} K^{-1}, estimated from the heat capacities[7] of C_2F_6 and C_2Br_6, we obtain $\Delta H_{r,298} = -161.3 \pm 3.0$ kJ mol^{-1}, whence follows $\Delta H^\circ_f[CF_2BrCF_2Br(gas)] = -789.9 \pm 4.0$ kJ mol^{-1}.

1-Bromo-1,1-difluoroethane

Pickard and Rodgers[100] measured the equilibrium constant of the reaction

$$CH_3CF_2Br\ (gas) + I_2\ (gas) \rightleftarrows CH_3CF_2I\ (gas) + IBr\ (gas) \qquad (23)$$

at 581–622 K and found [having estimated $\Delta S^\circ(23)$ and $\Delta C_p(23)$ by the method of group contributions] $\Delta H^\circ_{298}(23) = 42.7 \pm 0.8$ kJ. Adopting $\Delta H^\circ_f[IBr(gas)] = 40.80 \pm 0.14$ kJ mol^{-1} [21] and $\Delta H^\circ_f[CH_3CF_2I(gas)] = -410.0 \pm 8.5$ kJ mol^{-1} (see below), we obtain $\Delta H^\circ_f[CH_3CF_2Br(gas)] = -474.3 \pm 8.5$ kJ mol^{-1}.

Bromo-1,1,1-trifluoroethane

Buckley et al.[101] investigated the equilibrium

$$CF_3CH_2Br\ (gas) + I_2\ (gas) \rightleftarrows CF_3CH_2I\ (gas) + IBr\ (gas) \qquad (24)$$

in the range 614–726 K and calculated $\Delta H^\circ_{298}(24) = 27.6 \pm 2.1$ kJ on the basis of the Third Law of Thermodynamics using the thermodynamic functions of haloethanes taken from Ford[102]. Taking into account $\Delta H^\circ_f[CF_3CH_2I(gas)] = -648.6 \pm 3.9$ kJ mol^{-1} (see below), we obtain $\Delta H^\circ_f[CF_3CH_2Br(gas)] = -697.8 \pm 4.4$ kJ mol^{-1}.

Bromo-1,1,2,2-Tetrafluoroethane

Lacher et al.[46] measured the enthalpy of hydrobromination of gaseous perfluoroethylene and found $\Delta H^\circ_{r,367} = -137.7 \pm 0.9$ kJ mol^{-1}. Adopting $C_p[CHF_2CF_2Br(gas)] = 104.2$ J mol^{-1} K^{-1}, we find $\Delta H^\circ_{r,298} = -137.3 \pm 1$ kJ mol^{-1} and $\Delta H^\circ_f[CHF_2.CF_2Br(gas)] = -833.2 \pm 2.7$ kJ mol^{-1} from a comparison of the C_p for C_2H_6, C_2F_6, and C_2Br_6.[7]

1-Bromo-1-chloroethane

Bushneva et al.[103] investigated the equilibria in the thermocatalytic reactions of 1-bromo-1-chloroethane in the gas phase at 443–523 K and calculated the enthalpies of the following three reactions on the basis of the Second Law of Thermodynamics:

$$2CH_3CHClBr \rightleftarrows CH_3CHCl_2 + CH_3CHBr_2\ , \qquad (25)$$

$$CH_3CHClBr \rightleftarrows CH_2{=}CHCl + HBr\ , \qquad (26)$$

$$CH_3CHClBr \rightleftarrows CH_2{=}CHBr + HCl\ . \qquad (27)$$

They obtained $\Delta H^\circ_{483}(25) = 8.0 \pm 0.4$ kJ, $\Delta H^\circ_{483}(26) = 70.7 \pm 0.8$ kJ, and $\Delta H^\circ_{483}(27) = 66.1 \pm 1.7$ kJ. The above values were not adjusted to 298 K because of the lack of data for $C_p(CH_3CHClBr)$, but an approximate estimate of ΔC_p in reactions (25)–(27) showed that the difference between the values of ΔH°_{298} and ΔH°_{483} is less than the experimental error. Using the enthalpies of formation of chloro- and bromo-ethylenes quoted in Section II of the present review and also the ΔH°_f recommended above for CH_3CHCl_2 and CH_3CHBr_2, we obtain three values of $\Delta H^\circ_f[CH_3CHClBr(gas)]$: -82.6 ± 3.6, -84.1 ± 2.3, and -79.1 ± 3.4 kJ mol^{-1}. Their mean is recommended: $\Delta H^\circ_f[CH_3CHClBr(gas)] = -82.5$ kJ mol^{-1}. The error indicated takes into account the complexity of the composition of the equilibrium mixture and the actual discrepancies between the three results obtained[103].

1-Bromo-2-chloroethane

Bushneva et al.[104] found the enthalpies of the following reactions from measurements of their K_p at 483–523 K:

$$2CH_2ClCH_2Br\ (gas) \rightleftarrows CH_2ClCH_2Cl\ (gas) + CH_2BrCH_2Br\ (gas), \qquad (28)$$

$$CH_2ClCH_2Br\ (gas) \rightleftarrows CH_2{=}CHCl\ (gas) + HBr\ (gas), \qquad (29)$$

$$CH_2ClCH_2Br\ (gas) \rightleftarrows CH_2{=}CHBr\ (gas) + HCl\ (gas). \qquad (30)$$

They obtained $\Delta H^\circ_{503}(28) = 3.7 \pm 0.4$ kJ, $\Delta H^\circ_{503}(29) = 77.8 \pm 2.5$ kJ, and $\Delta H^\circ_{503}(30) = 69.0 \pm 2.1$ kJ. Neglecting the adjustment to the standard temperature, we obtain from these enthalpies three values of $\Delta H^\circ_f[CH_2ClCH_2Br(gas)]$: -88.1 ± 1.7, -91.2 ± 3.3, and -82.0 ± 2.8 kJ mol^{-1}. As in the case of 1-bromo-1-chloroethane, their average is recommended: $\Delta H^\circ_f[CH_2ClCH_2Br(gas)] = -87 \pm 5$ kJ mol^{-1}.

1,2-Dibromo-1,2-dichloroethane

Müller and Schumacher[105] determined the enthalpy of bromination of gaseous *trans*-dichloroethylene from the temperature dependence of the equilibrium constant in the range 343–373 K and obtained $\Delta H_{r,358} = -72.4 \pm 6$ kJ mol^{-1}. Using $C_p(CHClBrCHClBr) = 112.3$ J mol^{-1} K^{-1} estimated from the heat capacities of C_2H_6, C_2Cl_6, and C_2Br_6 quoted by Glushko[7], we find $\Delta H^\circ_{r,298} = -73.0 \pm 6$ kJ mol^{-1}, whence $\Delta H^\circ_f[CHClBr.CHClBr(gas)] = -36 \pm 6$ kJ mol^{-1}.

1,2-Dibromo-2-chloro-1,1,2-trifluoroethane

Lacher et al.[12] measured the enthalpy of bromination of gaseous chlorotrifluoroethylene: $\Delta H^\circ_{r,376} = -132.2 \pm 1.3$ kJ mol^{-1}. $C_p(CF_2BrCFClBr) = 124.9$ J mol^{-1} K^{-1} was adopted (from a comparison of the heat capacities of C_2F_6, C_2Cl_6, and C_2Br_6 quoted by Glushko[7]) in order to adjust the above quantities to 298 K. This yields $\Delta H^\circ_{r,298} = -132.6 \pm 1.3$ kJ mol^{-1}, whence follows $\Delta H^\circ_f[CF_2BrCFClBr(gas)] = -616.8 \pm 3.7$ kJ mol^{-1}.

1-Bromo-1-chloro-2,2,2-trifluoroethane

The enthalpy of combustion of 1-bromo-1-chloro-2,2,2-trifluoroethane, measured in a rotating bomb calorimeter[45], amounts to $\Delta H_c^\circ = -761.6 \pm 3.2$ kJ mol^{-1}. Hence $\Delta H_f^\circ[CF_3.CHClBr(liq.)] = -729.6 \pm 3.8$ kJ mol^{-1}. Taking into account the enthalpy of evaporation $\Delta H_{v,298}(CF_3CHClBr) = 29.69 \pm 0.1$ kJ mol^{-1} (the mean of two calorimetric determinations[45,106]), we obtain $\Delta H_f^\circ[CF_3CHClBr(gas)] = -699.9 \pm 3.8$ kJ mol^{-1}.

1-Bromo-2-chloro-1,1,2-trifluoroethane

The enthalpy of combustion of $CF_2BrCHFCl$ has been determined in a rotating bomb calorimeter at $\Delta H_c^\circ = -806.3 \pm 5.2$ kJ mol^{-1}.[45] Hence $\Delta H_f^\circ[CF_2BrCHFCl(liq.)] = -684.8 \pm 5.6$ kJ mol^{-1} or, when account is taken of the enthalpy of evaporation $\Delta H_{v,298}^\circ(CF_2BrCHFCl) = 30.15 \pm 0.1$ kJ mol^{-1},[107] one can obtain $\Delta H_f^\circ[CF_2BrCHFCl(gas)] = -654.7 \pm 5.6$ kJ mol^{-1}. The value found agrees with the measured[46] enthalpy of hydrobromination of chlorotrifluoroethylene when $\Delta H_f^\circ.[CF_2=CFCl(gas)] = 515.1 \pm 3.4$ kJ mol^{-1}, taken from Erastov and Kolesov[10], is used.

1-Bromo-2,2-dichloro-1,1-difluoroethane

Lacher et al.[46] measured the enthalpy of hydrobromination of 1,1-dichloro-2,2-difluoroethylene and obtained $\Delta H_{r,367} = 96.4 \pm 0.5$ kJ mol^{-1}. Having estimated $C_p(CF_2BrCHCl_2) = 114.1$ J mol^{-1} K^{-1} (from a comparison of the C_p for C_2H_6, C_2F_6, C_2Cl_6, and C_2Br_6 quoted by Glushko[7]), we find $\Delta H_{r,298}^\circ = -96.3$ kJ mol^{-1} and $\Delta H_f^\circ[CF_2BrCHCl_2(gas)] = -471 \pm 11$ kJ mol^{-1}.

The Difference between the Enthalpies of Formation of Bromoperfluoroethane and Pentafluoroethane

The equilibrium in the gas-phase reaction

$$C_2HF_5 + Br_2 \rightleftarrows C_2F_5Br + HBr \qquad (31)$$

was investigated[108,109] at temperatures in the range 632–860 K and $\Delta H_{746}^\circ(31) = -24.2 \pm 0.7$ kJ was found from the temperature variation of K_p. Buckley et al.[110] calculated $\Delta H_{298}^\circ(31) = -31.4 \pm 0.4$ kJ from the data of Coomber and Whittle[108] and Ferguson and Whittle[109] on the basis of the Third Law of Thermodynamics using the thermodynamic functions of C_2HF_5 and C_2F_5Br from Ford's dissertation[102]. The difference $\Delta H_f^\circ[C_2F_5Br(gas)] - \Delta H_f^\circ[C_2HF_5(gas)] = 35.9 \pm 0.5$ kJ mol^{-1} corresponds to the above value.

The Difference between the Enthalpies of Formation of Bromo- and Chloro-Perfluoroethanes

Coomber and Whittle[111] investigated the equilibrium

$$C_2F_5Br\,(gas) + Cl_2\,(gas) \rightleftarrows C_2F_5Cl\,(gas) + BrCl\,(gas) \qquad (32)$$

at 738–833 K and calculated $\Delta H_{785}^\circ(32) = -43.3 \pm 1.1$ kJ on the basis of the Second Law of Thermodynamics. Buckley et al.[110] calculated from the same data $\Delta H_{298}^\circ(32) = -39.75 \pm 0.4$ kJ on the basis of the Third Law of Thermodynamics. Hence we find the difference $\Delta H_f^\circ[C_2F_5Br(gas)] - \Delta H_f^\circ[C_2F_5Cl.(gas)] = 54.5 \pm 0.4$ kJ mol^{-1}.

Iodoethane

Measurements of the enthalpy of combustion of iodoethane by Thomsen[69] and Berthelot[112] as well as the determination of the ΔH of the substitution of iodine by bromine in iodoethane[68] are at present only of historical interest. Springall and White[113] determined the enthalpy of combustion of liquid iodoethane and obtained $\Delta H_c^\circ = -1466.5 \pm 2.1$ kJ mol^{-1}; hence $\Delta H_f^\circ[C_2H_5I(liq.)] = -35.1 \pm 2.1$ kJ mol^{-1} and, when account is taken of $\Delta H_{v,298}^\circ(C_2H_5I) = 32.2 \pm 0.4$ kJ mol^{-1},[7] we obtain $\Delta H_f^\circ[C_2H_5I(gas)] = -2.9 \pm 2.1$ kJ mol^{-1}. One should note that Springall and White[113] give no information about the purity of the specimen, the results of the analysis of the combustion products, and the number of experiments.

Carson et al.[114] measured the enthalpies of iodination of solutions of diethylzinc and diethylcadmium in benzene and ether respectively and also the enthalpies of solution of iodine in benzene and ether. Neglecting the enthalpies of solution of iodoethane in benzene and ether and using the values of ΔH_f° for diethylzinc, diethylcadmium, and the corresponding metal iodides adopted by Glushko[7], we obtain from these data two values of $\Delta H_f^\circ[C_2H_5I(liq.)]$, which are respectively -40.6 and -39.7 kJ mol^{-1}. Their reliability is reduced owing to the inadequately rigorous allowance for the heats of side reactions.

Ashcroft et al.[93] measured the enthalpy of reduction of ethyl iodide by lithium hydride in an ethereal solution of lithium tetrahydroaluminate, whence the heat of the reaction

$$C_2H_5I\,(liq.) + {}^1/_2H_2\,(gas) = C_2H_6\,(gas) + {}^1/_2I_2\,(cryst.) \qquad (33)$$

was found to be $\Delta H_{298}^\circ(33) = -44.3 \pm 0.7$ kJ. This value leads to $\Delta H_f^\circ[C_2H_5I(liq.)] = -39.7 \pm 0.8$ kJ mol^{-1} and $\Delta H_f^\circ.[C_2H_5I(gas)] = -7.5 \pm 0.9$ kJ mol^{-1}. We believe that this latter value is the most reliable.

1,2-Di-iodoethane

The equilibrium constants of the reaction

$$CH_2ICH_2I\,(gas) \rightleftarrows C_2H_4\,(gas) + I_2\,(gas) \qquad (34)$$

have been measured[115–118] at 282–476 K). The results of Mooney and Ludlam[115] are doubtful, since their measurements were performed at I_2 and $C_2H_4I_2$ concentrations close to saturation. The other data[116–118] agree satisfactorily. Benson and Amano[118] subjected them to a joint treatment on the basis of the Second Law of Thermodynamics and obtained $\Delta H_{380}^\circ(34) = 48.12 \pm 0.84$ kJ. Adjustment to the standard temperature leads to $\Delta H_{298}^\circ(34) = 48.16 \pm 0.84$ kJ, whence $\Delta H_f^\circ[CH_2ICH_2I(gas)] = 66.7 \pm 1.0$ kJ mol^{-1}.

Tetrafluoro-1,2-di-iodoethane

Wu and Rodgers[119] investigated the equilibrium

$$CF_2{=}CF_2\,(gas) + I_2\,(gas) \rightleftarrows CF_2ICF_2I\,(gas) \qquad (35)$$

at 477–562 K and calculated $\Delta H_{520}^\circ(35) = -66.5 \pm 2.1$ kJ on the basis of the Second Law of Thermodynamics. Adjustment to 298 K, which the authors carried out themselves[119], led to $\Delta H_{298}^\circ(35) = -69.5 \pm 2.1$ kJ. Hence it follows that $\Delta H_f^\circ[CF_2I.CF_2I(gas)] = -666.6 \pm 3.3$ kJ mol^{-1}.

1,1-Difluoro-1-iodoethane

Pickard and Rodgers[100] quote the difference between the enthalpies of formation of 1,1-difluoro-1-iodoethane and 1,1-difluoroethane given previously in Pickard's dissertation[120]:

$[\Delta H_f^0(CH_3CF_2I\ (gas)) - \Delta H_f^0(CH_3CHF_2\ (gas))]_{298} = 87.0 \pm 0.8$ kJ mol^{-1}

Using the value of $\Delta H_f^\circ(CH_3CHF_2)$ recommended above, we find $\Delta H_f^\circ[CH_3CF_2I(gas)] = -410.0 \pm 8.5$ kJ mol^{-1}.

1,1,1-Trifluoroiodoethane

Wu and Rodgers[121] measured the equilibrium constant of the reaction

$$CF_3CH_3\,(r) + I_2\,(r) \rightleftarrows CF_3CH_2I\,(r) + HI\,(r) \qquad (36)$$

at 730–775 K. Having estimated the entropies of haloethanes, the above workers[121] calculated $\Delta H_{298}^\circ(36) = 64.0 \pm 2.1$ kJ on the basis of the Third Law of Thermodynamics. Hence, taking into account the value of $\Delta H_f^\circ[CH_3CF_3(gas)]$ recommended above, we obtain $\Delta H_f^\circ[CF_3CH_2I(gas)] = -648.6 \pm 3.9$ kJ mol^{-1}.

1-Bromo-2-Iodoethane

Berthelot[68] measured the enthalpy of the reaction

$$CH_2ICH_2I\ (cryst.) + Br_2\ (liq.) = CH_2BrCH_2I\ (cryst.) + BrI\ (cryst.) \qquad (37)$$

and obtained $\Delta H(37) = -58.2$ kJ. In view of the lack of more accurate measurements of $\Delta H_f^\circ(CH_2BrCH_2I)$, we calculated this quantity from Berthelot's data[68]. Using $\Delta H_f^\circ[IBr(cryst.)] = -10.33$ kJ mol^{-1} and $\Delta H_{S,298}^\circ(CH_2ICH_2I) = 66.9$ kJ mol^{-1} taken from Glushko's handbook[7] as well as the value of $\Delta H_f^\circ[CH_2I.CH_2I(gas)]$ recommended above, we find $\Delta H_f^\circ[CH_2ICH_2Br.(cryst.)] = -48.1$ kJ mol^{-1}. Adopting $\Delta H_{S,298}^\circ(CH_2BrCH_2I) = 60.3$ kJ mol^{-1} [the mean of the two values of $\Delta H_{S,298}^\circ(CH_2I.CH_2I)$ presented above and $\Delta H_{S,283}^\circ(CH_2BrCH_2Br) = 53.6$ kJ mol^{-1}[7]], we obtain $\Delta H_f^\circ[CH_2BrCH_2I(gas)] = 12.2$ kJ mol^{-1}; this value is only approximate.

The Difference between the Enthalpies of Formation of Iodo- and Bromo-perfluoroethanes

Buckley et al.[110] studied the equilibrium

$$C_2F_5Br + I_2 \rightleftarrows C_2F_5I + IBr \qquad (38)$$

in the gas phase at 618–667 K. Using the thermodynamic functions of haloethanes calculated by Ford[102], Buckley et al.[110] obtained $\Delta H_{298}^\circ(38) = 38.5 \pm 0.8$ kJ. Hence we obtain the difference $\Delta H_f^\circ[C_2F_5I(gas)] - \Delta H_f^\circ[C_2F_5Br(gas)] = 60.1 \pm 0.8$ kJ mol^{-1}.

V. ESTIMATION OF THE ENTHALPIES OF FORMATION OF HALOETHANES

Among the numerous additive methods whereby the enthalpies of formation of organic compounds can be calculated approximately, only a few have been used to estimate the ΔH_f° of haloethanes. The enthalpies of formation were usually estimated only for a small number of haloethanes. All the haloethanes were never embraced by a single computational scheme sufficiently accurate in relation to this particular group of substances.

Rodgers[122] used Zahn's method[123] for the calculation of the enthalpies of formation of chlorofluorocarbons and evaluated six constants of the additive scheme whereby it is possible to calculate the ΔH_f° for only ten haloethanes. Furthermore some of the experimental ΔH_f° used by Rodgers[122] to calculate the constants are now obsolete. The attempt by Lacher and Skinner[124] to apply Allen's scheme[125] to fluoro- and chloro-derivatives of methane and ethane did not yield satisfactory results owing to the small number of experimental data available at the time. Later Gasteiger et al.[126] used Allen's scheme to estimate the enthalpies of formation of haloalkanes having at their disposal more extensive experimental data. Constants were found for the calculation of the ΔH_f° for mono- and poly-chloro-substituted hydrocarbons and also mono-fluoro-, monobromo-, and monoiodo-derivatives; only a small proportion of the haloethanes are included in the above groups of substances.

The "incremental" method used by Andreevskii et al.[127] for fluoroalkanes makes it possible to calculate the enthalpies of formation of substances containing substituent atoms of only two types. Benson et al.[128], who proposed the method of "group contributions" for the calculation of ΔH_f°, evaluated the contributions of 12 halogen-containing groups with the aid of which it is possible in principle to find the enthalpies of formation of 78 haloethanes. However, it has been noted by several workers[60,128] that the method of group contributions leads to highly distorted estimates for compounds containing adjacent groups with sharply different polarities, which is in fact a characteristic feature of a large number of haloethanes.

According to the scheme developed by Somayajulu and Zwolinski[129,130], the enthalpies of formation of haloethanes are calculated as sums of contributions corresponding to the interactions in sets of three atoms linked to a single carbon atom and to "excess" vicinal interactions. Somayajulu and Zwolinskii[130] quote constants whereby it is possible to estimate the ΔH_f° for 78 haloethanes, but some of the experimental ΔH_f° used in their study have now been modified. The calculation of the constants of the scheme of Somayajulu and Zwolinski constitutes a fairly cumbersome procedure in view of the need to calculate the number of sets of three atoms and vicinal interactions.

Bernstein[13,14] proposed a method for the estimation of the enthalpies of formation based on the allowance for the pair interactions of all the atoms in the molecule both linked and not linked by chemical bonds. In the estimation of the ΔH_f° for haloethanes in Bernstein's later study[14], the initial scheme was simplified: the group $-CH_3$ was regarded as one of the substituents in methane and the enthalpies of formation of haloethanes not containing the CH_3 group were calculated as the sums of the contributions of two substituted methyl groups. In this approach no account was taken of the fairly intense interactions of the substituents in haloethanes located at different carbon atoms. This simplification, made in view of the limited number of experimental data, led to a significant decrease of the accuracy of the estimate. Discrepancies are particularly large between the ΔH_f° calculated by Bernstein[14] and subsequently determined experimentally for fluoroethanes.

Nevertheless the method proposed by Bernstein is in principle extremely promising for compounds with a short carbon chain and different substituents, since it makes it possible to estimate the enthalpies of formation with a satisfactory accuracy using a comparatively small number of constants in the computational formulae. In combination with modern experimental data, this method has been applied successfully to the estimation of ΔH_f° for halomethanes[8,21] and fluoroethylenes[21].

In the present review Bernstein's method was used for the approximate calculation of the enthalpies of formation of haloethanes. Since the experimental data accumulated at the present time make it possible to take into account all the pair interactions of the atoms in haloethanes (except in the case of iodo-derivatives) and in order to facilitate calculations,

the computational formulae were modified compared with those proposed by Bernstein[13,14].

The enthalpy of formation of a haloethane containing substituents of only two types (X and Y) can be represented, according to Bernstein, by the sum of the following contributions: $P(CC)_1$, $P(CX)_1$, $P(CY)_1$, $P(CX)_2$, $P(CY)_2$, $P(XX)_2$, $P(YY)_2$, $P(XY)_2$, $P(XX)_3$, $P(YY)_3$, and $P(XY)_3$. Subscript 1 refers to a pair of atoms connected by chemical bond, subscript 2 refers to atoms linked by two bonds, and subscript 3 refers to atoms joined by three bonds. Since the numbers of contributions are not linearly independent, they can be reduced to the following four constants of the computational scheme:

$$[CX]_1 = {}^1/_6 P(CC)_1 + P(CX)_1 + P(CX)_2 + P(XX)_2 + {}^3/_2 P(XX)_3 , \quad (39)$$

$$[CY]_1 = {}^1/_6 P(CC)_1 + P(CY)_1 + P(CY)_2 + P(YY)_2 + {}^3/_2 P(YY)_3 , \quad (40)$$

$$[XY]_2 = P(XY)_2 - {}^1/_2 [P(XX)_2 + P(YY)_2] , \quad (41)$$

$$[XY]_3 = P(XY)_3 - {}^1/_2 [P(XX)_3 + P(YY)_3] . \quad (42)$$

The linear combinations (39–(42) were selected so that the evaluation of ΔH_f° requires the calculation of only the number of bonds between carbon atoms and substituents and the number of interactions between unlike substituent atoms.

Table 1. Experimental and calculated enthalpies of formation of haloethanes at 298.15 K.

No.	Compound	$-\Delta H_f^0$ (gas), kJ mol^{-1}		Refs.*
		expt.	calc.	
1	CH_3CH_3	84.0±0.4	83.2	[52, 53]
2	CF_3CF_3	1344.0±4.0	1345.1	[21]
3	CH_3CHF_2	497.0±8.5	502.6	[32]
4	CH_3CF_3	748.7±3.2	744.8	[59]
5	CH_2FCHF_2	691±10	688.0	[11]
6	CCl_3CCl_3	(137.7; 145.2; 138; 150.9)**	149.5	—
7	CH_3CH_2Cl	112.2±0.7	111.1	[39]
8	CH_3CHCl_2	130.6±3.0	131.1	[75]
9	CH_2ClCH_2Cl	134.1±1.2	133.2	[77]
10	CH_3CCl_3	144.6±0.8	142.9	[25, 79]
11	$CH_2ClCHCl_2$	144.7±1.9	147.2	[82]
12	CH_2ClCCl_3	152.3±1.4	153.2	[83]
13	$CHCl_2CHCl_2$	157.3±3.0	155.3	[67]
14	$CHCl_2CCl_3$	(137.9; 143.1; 145.8)	155.4	—
15	CF_2ClCF_2Cl	925.5±4.3	925.8	[87]
16	$CF_2ClCFCl_2$	726.8±2.8	724.1	[43]
17	CF_2ClCCl_3	525.8±4.3	527.9	[90]
18	CH_3CHFCl	313.4±2.6	314.1	[91]
19	CH_3CF_2Cl	536.2±5.2	538.6	[92]
20	CH_3CH_2Br	61.5±1.0	63.7	[49, 71]
21	CH_3CHBr_2	26.7±1.9	26.7	[97, 98]
22	CH_2BrCH_2Br	38.3±1.2	33.1	[78, 97, 98]
23	CF_2BrCF_2Br	789.9±4.0	800.7	[12]
24	CH_3CF_2Br	474.3±8.5	472.8	[100]
25	CF_3CH_2Br	697.8±4.4	703.7	[101]
26	CHF_2CF_2Br	833.2±2.7	846.2	[46]
27	$CH_3CHClBr$	82±5	80.9	[103]
28	CH_2ClCH_2Br	87±5	82.1	[104]
29	$CHClBrCHClBr$	36±6	44.6	[105]
30	$CF_2BrCFClBr$	616.8±3.7	602.5	[12]
31	$CF_3CHClBr$	699.9±3.8	698.1	[45]
32	$CF_2BrCHFCl$	654.7±5.6	655.9	[45]
33	$CF_2BrCHCl_2$	471±11	471.4	[46]
34	$[\Delta H_f^0(C_2F_5Br) - \Delta H_f^0(C_2HF_5)]$	35.9±0.5	43.9	[108, 109]
35	$[\Delta H_f^0(C_2F_5Br) - \Delta H_f^0(C_2F_5Cl)]$	54.5±0.4	59.8	[111]
36	CH_3CH_2I	7.5±0.9	—	[93]
37	CH_2ICH_2I	−66.7±1.0	—	[116–118]
38	CF_2ICF_2I	666.6±3.3	—	[119]
39	CH_3CF_2I	410.0±8.5	—	[100]
40	CF_3CH_2I	648.6±3.9	—	[121]
41	CH_2BrCH_2I	(−12.2)	—	[68]
42	$[\Delta H_f^0(C_2F_5I) - \Delta H_f^0(C_2F_5Br)]$	60.1±0.8	—	[110]

* References are given only to studies which served as a basis for the recommended ΔH_f°.

** Here and henceforth the experimental values regarded as unreliable are given in brackets.

For example, the enthalpy of formation of 1,1,2-trifluoroethane can be represented by the following sum:

$$\Delta H_f^\circ(CH_2FCHF_2) = 3[CH]_1 + 3[CF]_1 + 4[HF]_2 + 5[HF]_3 .$$

Thus, in order to calculate the ΔH_f° for ten haloethanes having the composition $C_2X_{6-n}Y_n$ (where $0 \leq n \leq 6$), it is necessary to know four constants. When a third substituent (Z) is introduced, a further five constants must be added: $[CZ]_1$, $[XZ]_2$, $[XZ]_3$, $[YZ]_2$, and $[YZ]_3$, which are defined by relations analogous to Eqns.(39)–(42); having calculated them, it is possible to evaluate the enthalpies of formation of 55 haloethanes having the composition $C_2X_{6-m-n}Y_mZ_n$. When there are substituents of four types, 16 constants are necessary to estimate the ΔH_f° for 210 compounds. When a fifth substituent is introduced, the number of haloethanes increases to 630 and the number of constants rises to 25.

The available set of experimental data makes it possible to calculate the 16 constants necessary to estimate the ΔH_f° for ethanes containing H, F, Cl, and Br. The following numerical constants (in kJ mol^{-1}) were found by the method of least squares from the recommended experimental values listed in Table 1 (with the exception of ΔH_f° for C_2Cl_6 and C_2HCl_5 as well as iodoethanes): $[CH]_1 = -14.488$, $[CF]_1 = -223.266$, $[CCl]_1 = -23.897$, $[CBr]_1 = +33.523$, $[HF]_2 = +12.858$, $[HF]_3 = -3.444$, $[HCl]_2 = -3.916$, $[HCl]_3 = -3.151$, $[HBr]_2 = -6.880$, $[HBr]_3 = -3.672$, $[FCl]_2 = +2.920$, $[FCl]_3 = +1.018$, $[FBr]_2 = +7.675$, $[FBr]_3 = -1.351$, $[ClBr]_2 = -1.273$, and $[ClBr]_3 = +1.448$. These constants were used to estimate the enthalpies of formation of bromoethanes listed in Tables 1 and 2.

It is noteworthy that the recommended values of ΔH_f° for haloethanes containing only H, F, and Cl are as a rule the most reliable: the availability of numerous experimental data made it possible to select the most accurate values confirmed by several workers. In this connection, it is possible to obtain also more accurate estimates of ΔH_f° for ethanes containing H, F, and Cl. For this purpose, 17 experimental values of ΔH_f° for ethanes containing H, F, and Cl (except for C_2Cl_6 and C_2HCl_5) were treated by the method of least squares, which yielded the following nine constants (in kJ): $[CH]_1 = -13.859$, $[CF]_1 = -224.190$, $[CCl]_1 = -24.915$, $[HF]_2 = +10.786$, $[HF]_3 = -3.401$, $[HCl]_2 = -4.038$, $[HCl]_3 = -2.952$, $[FCl]_2 = +2.753$, and $[FCl]_3 = +2.444$. The enthalpies of formation of chlorofluoroethanes listed in Tables 1 and 3 were calculated with the aid of the above constants.

The nine constants for the estimation of ΔH_f° for ethanes containing H, F, and I or the 16 constants for the estimation of ΔH_f° for ethanes with H, F, Br, and I can also be found in principle from the available experimental data (Table 1). However, the number of experimental values of ΔH_f° for iodoethanes which serve as reference values for the calculation of constants referring to interactions of the iodine atom with other atoms, namely $[CI]_1$, $[HI]_2$, $[HI]_3$, $[FI]_2$, etc., is equal to the number of the required constants and such a system of equations would be ill-founded. Further accumulation of experimental data is therefore necessary for the estimation of the unknown ΔH_f° for iodoethanes.

VI. CONCLUSION

The calculated ΔH_f° for haloethanes are compared in Table 1 with the recommended experimental values. The average discrepancy between the experimental and calculated values for chlorofluoroethanes is 1.9 kJ mol^{-1}, while for the bromo-derivatives it is much higher (5.3 kJ mol^{-1}), which was to be expected in view of the lower accuracy of the experimental

data. Comparison of the experimental and calculated values (Table 1) suggests that the errors of the estimated ΔH_f° for ethanes containing H, F, and Cl (Table 3) do not exceed 5–10 kJ mol^{-1}, while those for bromine-containing ethanes (Table 2) are not more than 20–25 kJ mol^{-1}.

Table 2. Calculated enthalpies of formation of bromoethanes (kJ mol^{-1}) at 298.15 K.

No.	Compound	$-\Delta H_f^0$ (gas)	No.	Compound	$-\Delta H_f^0$ (gas)
1	CBr_3CBr_3	—201.1	27	CH_2FCBr_3	152.0
2	CH_3CBr_3	—24.1	28	$CHBr_2CHFBr$	168.9
3	$CH_2BrCHBr_2$	—11.2	29	$CFBr_2CH_2Br$	173.0
4	CH_2BrCBr_3	—69.3	30	$CHFBrCF_3$	874.8
5	$CHBr_2CHBr_2$	—62.9	31	CHF_2CFBr_2	592.4
6	$CHBr_2CBr_3$	—128.4	32	$CHFBrCF_2Br$	602.9
7	CF_3CF_2Br	1071.5	33	CF_3CHBr_2	649.4
8	CF_3CFBr_2	818.8	34	$CHBr_2CF_2Br$	374.8
9	CF_3CBr_3	581.4	35	$CHFBrCFBr_2$	346.3
10	$CF_2BrCFBr_2$	545.3	36	CBr_3CHF_2	353.9
11	CF_2BrCBr_3	305.2	37	$CHBr_2CFBr_2$	115.6
12	$CFBr_2CFB_2$	287.1	38	$CHFBrCBr_3$	105.1
13	$CFBr_2CBr_3$	44.4	39	CCl_3CCl_2Br	84.2
14	CH_3CHFBr	255.4	40	CCl_3CClBr_2	22.4
15	CH_2FCH_2Br	251.3	41	CCl_2BrCCl_2Br	27.8
16	$CH_2FCHFBr$	436.1	42	CCl_3CBr_3	—41.9
17	CH_2BrCHF_2	464.7	43	$CCl_2BrCClBr_2$	—31.0
18	CH_3CFBr_2	216.7	44	CCl_2BrCBr_3	—92.4
19	CH_2FCHBr_2	208.6	45	$CClBr_2CClBr_2$	—87.0
20	$CH_2BrCHFBr$	219.0	46	$CClBr_2CBr_3$	—145.5
21	CHF_2CHFBr	642.6	47	CH_3CCl_2Br	90.2
22	CF_2BrCH_2F	646.7	48	$CH_2ClCHClBr$	93.0
23	CH_2FCFBr_2	391.7	49	$CH_2BrCHCl_2$	92.7
24	CH_2BrCF_2Br	430.7	50	CH_3CClBr_2	34.3
25	$CHFBrCHFBr$	398.1	51	$CH_2ClCHBr_2$	36.9
26	CHF_2CHBr_2	416.1	52	$CH_2BrCHClBr$	42.0
53	CCl_3CH_2Br	95.5	79	CCl_3CF_2Br	458.9
54	$CHCl_2CHClBr$	97.3	80	$CFCl_2CFClBr$	464.9
55	CCl_2BrCH_2Cl	96.0	81	CCl_2BrCF_2Cl	478.6
56	$CH_2ClCClBr_2$	38.2	82	$CF_2ClCClBr_2$	424.5
57	CH_2BrCCl_2Br	43.1	83	CF_2BrCCl_2Br	410.2
58	$CHCl_2CHBr_2$	39.2	84	$CFClBrCFClBr$	406.4
59	CH_2ClCBr_3	—22.2	85	$CFCl_2CFBr_2$	401.0
60	$CHBr_2CHClBr$	—10.6	86	CF_2ClCBr_3	367.8
61	$CClBr_2CH_2Br$	—11.8	87	$CFBr_2CFClBr$	345.3
62	$CHCl_2CCl_2Br$	94.0	88	$CClBr_2CF_2Br$	359.0
63	$CHClBrCCl_3$	93.7	89	$CFCl_2CCl_2Br$	278.5
64	$CHCl_2CClBr_2$	34.2	90	$CFClBrCCl_3$	268.6
65	$CHClBrCCl_2Br$	39.4	91	$CFCl_2CClBr_2$	220.5
66	CCl_3CHBr_2	33.7	92	$CFClBrCCl_2Br$	216.1
67	$CHBr_2CCl_2Br$	—17.8	93	CCl_3CFBr_2	200.8
68	$CHClBrCClBr_2$	—17.5	94	$CFBr_2CCl_2Br$	151.2
69	CBr_3CHCl_2	—28.1	95	$CFClBrCClBr_2$	161.1
70	$CHBr_2CClBr_2$	—71.8	96	CBr_3CFCl_2	160.0
71	$CHClBrCBr_3$	—77.0	97	$CFBr_2CClBr_2$	99.1
72	$CF_3CFClBr$	875.1	98	$CFClBrCBr_3$	103.5
73	CF_2ClCF_2Br	861.5	99	$CH_3CFClBr$	278.6
74	CF_3CCl_2Br	684.6	100	$CH_2FCHClBr$	260.9
75	$CF_2ClCFClBr$	667.1	101	$CH_2ClCHFBr$	266.2
76	$CF_2BrCFCl_2$	657.3	102	$CH_2BrCHFCl$	275.8
77	CF_3CClBr_2	634.2	103	$CH_2FCFClBr$	451.7
78	$CF_2ClCFBr_2$	606.9	104	CH_2ClCF_2Br	482.4
105	CH_2BrCF_2Cl	495.1	124	CHF_2CClBr_2	408.5
106	$CHF_2CHClBr$	466.6	125	$CHFClCFBr_2$	400.2
107	$CHFClCHFBr$	453.0	126	$CHFBrCFClBr$	405.4
108	CH_2FCCl_2Br	262.6	127	$CHClBrCF_2Br$	424.4
109	$CH_2ClCFClBr$	283.1	128	$CHBr_2CF_2Cl$	438.3
110	$CH_2BrCFCl_2$	292.4	129	$CHFClCCl_2Br$	274.4
111	$CHClBrCHFCl$	20.79	130	$CHFBrCCl_3$	264.3
112	$CHFBrCHCl_2$	278.2	131	$CHClBrCFCl_2$	289.3
113	$CH_2FCClBr_2$	203.2	132	$CFClBrCHCl_2$	279.8
114	$CH_2ClCFBr_2$	219.2	133	$CHFClCClBr_2$	218.5
115	$CH_2BrCFClBr$	234.0	134	$CHFBrCCl_2Br$	213.0
116	$CHFClCHBr_2$	224.7	135	$CHClBrCFClBr$	229.0
117	$CHFBrCHClBr$	220.3	136	$CHCl_2CFBr_2$	213.9
118	$CHF_2CFClBr$	650.6	137	$CHBr_2CFCl_2$	236.9
119	$CHFBrCF_2Cl$	665.4	138	$CHFClCBr_3$	159.9
120	CHF_2CCl_2Br	460.7	139	$CHFBrCClBr_2$	160.7
121	$CHFClCFClBr$	462.2	140	$CHClBrCFBr_2$	166.0
122	$CHFBrCFCl_2$	462.0	141	$CHBr_2CFClBr$	175.6
123	$CHClBrCF_2Cl$	490.8			

The calculated ΔH_f° obey certain relations noted previously. Thus there is a sharp increase of $|\Delta H_f^\circ|$ in the series $C_2H_{6-n}F_n$, $C_2Cl_{6-n}F_n$, $C_2Br_{6-n}F_n$ as fluorine atoms accumulate at the same carbon atom, as in the case of other organofluorine compounds[3,89,131]. In the $C_2H_{6-n}Cl_n$ series there is also an increase of ΔH_f° with increase of n, but there is a maximum at $n = 4$. A similar picture has been noted for chloromethanes where the maximum value of $|\Delta H_f^\circ|$ corresponds to $CHCl_3$.[3]

On successive replacement of hydrogen by bromine in the $C_2H_{6-n}Br_n$ series, a more rapid increase of ΔH_f° is observed than would have been the case for a linear relation between ΔH_f° and n. This is also characteristic of bromomethanes[3].

Table 3. Calculated enthalpies of formation of chlorofluoroethanes (kJ mol^{-1}) at 298.15 K.

No.	Compound	$-\Delta H_f^0$ (gas)	No.	Compound	$-\Delta H_f^0$ (gas)
1	CH_3CH_2F	282.1	20	CHF_2CHFCl	702.4
2	CH_3FCH_2F	474.3	21	CF_2ClCH_2F	715.2
3	CH_2FCF_3	923.3	22	CH_2FCFCl_2	512.6
4	CHF_2CHF_2	894.9	23	CH_2ClCF_2Cl	543.1
5	CHF_2CF_3	1123.4	24	$CHFClCHFCl$	514.7
6	CCl_3CCl_3	149.5	25	CHF_2CHCl_2	515.4
7	$CHCl_2CCl_3$	155.4	26	CCl_3CH_2F	315.5
8	CF_3CF_2Cl	1133.0	27	$CHCl_2CHFCl$	332.6
9	CF_3CFCl_2	926.4	28	$CFCl_2CH_2Cl$	345.4
10	CF_3CCl_3	725.3	29	CHF_2CF_2Cl	913.3
11	$CFCl_2CFCl_2$	527.3	30	$CHFClCF_3$	928.8
12	$CFCl_2CCl_3$	336.0	31	CHF_2CFCl_2	708.7
13	CH_2FCH_2Cl	301.3	32	$CHFClCF_2Cl$	723.7
14	$CH_2FCHFCl$	497.5	33	CF_3CHCl_2	739.9
15	CH_2ClCHF_2	513.0	34	$CHCl_2CF_2Cl$	539.5
16	CH_3CFCl_2	338.0	35	$CHFClCFCl_2$	524.0
17	CH_3FCHCl_2	312.4	36	CCl_3CHF_2	509.6
18	$CH_2ClCHFCl$	327.4	37	$CHCl_2CFCl_2$	344.7
19	CF_3CH_2Cl	746.4	38	$CHFClCCl_3$	329.7

Further development of the thermochemistry of haloethanes involves the accumulation of reliable experimental data. Thus very few values of ΔH_f° are available at present for iodoethanes and there are no data whatever for haloethanes containing Cl and I. The number of known values of ΔH_f° for bromoethanes is clearly inadequate and the reliability of some of the available data is low. As regards the haloethanes containing H, F, and C atoms, which are of greatest importance in practice, some of the values measured previously (for example, for C_2Cl_6, and C_2HCl_5) must also be checked experimentally and the number of reliable experimental data must be increased. All these considerations will permit an improvement in the accuracy of the estimates of ΔH_f° and will give rise to more reliable thermochemical parameters for all haloethanes.

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Diazotisation of Weakly Basic Aromatic and Heterocyclic Amines in Strongly Acid Media

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The review is devoted to the diazotisation of weakly basic aromatic amines. The methods of synthesis of diazonium salts based on these amines by non-traditional methods are examined. Data on the mechanism of the diazotisation reaction in strongly acid media are surveyed. Reactions of diazonium salts leading to the synthesis of new compounds are presented. The bibliography includes 75 references.

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I. INTRODUCTION

The diazotisation reaction has been known for a long time in organic chemistry. Diazotisation in weakly acid aqueous solutions has been particularly thoroughly investigated. Diazonium salts, used to synthesise a wide variety of different classes of compounds, are obtained in this way from strongly and moderately basic amines. Thus all possible azo-products, including azo-dyes, have been synthesised by a reaction without evolution of nitrogen. Reactions with evolution of nitrogen lead to functional derivatives of aromatic compounds. The reaction involving the substitution of the diazo-group by a metal has been developed by the school of Academician A.N.Nesmeyanov.

The diazotisation of weakly basic amines, which in the present review are understood as aromatic amines containing electronegative groups in the nucleus, has been much less well studied. The diazotisation of such compounds is as a rule carried out in strongly acid media. There are a number of reasons for this. The most inert amines, such as 2,4,6-trinitroaniline[1] or 6-bromo-2,4-dinitroaniline[2], are not diazotised under other conditions. Many diazonium salts containing strongly electronegative substituents, for example, 2,4,6-trinitrobenzenediazonium[3] or 3-carboxypyrazole-4-diazonium[4] sulphates are stable only in concentrated acids, decomposing on dilution with water, frequently with substitution of the diazo-group by the hydroxy-group[4]. A high acid concentration hinders, as a result of the protonation of the amino-group, the formation of 1,3-disubstituted triazenes from the diazonium salt and the initial amine in the course of the reaction[5-8].

The range of reactions of the diazonium salts obtained from weakly basic amines is limited, which we believe to be due to the inadequate attention devoted to the diazotisation of such amines.

The necessity to analyse the literature data and to describe them systematically has arisen in view of the possibility of employing weakly basic amines in the diazotisation reaction, which can lead to the synthesis of many substances of practical value which are otherwise difficult to obtain.

II. THE MECHANISM OF DIAZOTISATION IN STRONGLY ACID MEDIA

The present understanding of the diazotisation reaction of aromatic and heterocyclic amines is based on the consideration of four stages in the process[9,10]:

$$ArNH_2 + NOX \rightleftarrows ArNH_2^{\oplus}NO + X^{\ominus}, \quad (1)$$

$$ArNH_2NO^{\oplus} \underset{+H^{\oplus}}{\overset{-H^{\oplus}}{\rightleftarrows}} ArNHNO, \quad (2)$$

$$ArNHNO \rightleftarrows Ar{-}N{=}N{-}OH, \quad (3)$$

$$Ar{-}N{=}N{-}OH \begin{cases} \xrightarrow{HX} ArN_2^{\oplus}X^{\ominus} + H_2O, \\ \longrightarrow ArN_2^{\oplus}OH^{\ominus}. \end{cases} \quad (4)$$

In diazotisation in dilute acid solutions the rate-determining stage is the first—involving reaction with the nitrosating agent NOX with formation of a nitrosoammonium ion, which, being a strong acid[11], is readily deprotonated to the nitrosoamine. It is extremely probable that both stages can occur simultaneously.

In the third stage the nitrosoamine undergoes a tautomeric rearrangement to the diazohydrate†, which instantaneously gives rise to the diazonium cation [stage (4)].

The reaction in a strongly acid medium is distinguished by a high reactivity of the diazotising agent and a high rate of nitrosation. Nitrosonium sulphate (nitrosylsulphuric acid), which consists of ionic components, is usually employed as the nitrosating agent[12]. The generation of active nitrosonium cations has been demonstrated by ultraviolet spectroscopy of solutions in sulphuric acid[13]:

$$HNO_2 + 2H_2SO_4 \rightleftarrows NO^{\oplus} + H_3O^{\oplus} + 2HSO_4^{\ominus}.$$

In terms of its activity, the nitrosonium cation exceeds all known nitrosating agents[9]:

$$NO^{\ominus} > \begin{matrix} H \\ H \end{matrix}\!\!>\!O^{\oplus}{-}NO > BrNO > ONONO > HONO.$$

Kinetic studies have shown that in a strongly acid medium the *N*-nitrosation stage does not determine the reaction rate. It has been suggested[14] that an arylamine is rapidly nitrosated to give a low equilibrium concentration of the nitrosoammonium ion, which is converted into the diazonium ion with a slow transfer and elimination of protons. These two stages determine the rate of diazotisation in a strongly acid medium.

With increase of the acidity of the medium, the equilibrium concentration of the nitrosoammonium ion and the rate of loss of a proton diminish.

† Not isolated hitherto[9].

It is noteworthy that the formation of nitrosoammonium salts is possible also in reactions with weak acids, for example, in the reaction of nitrous acid with acetic acid or acetic anhydride[15]:

$$HNO_2 + AcOY \rightleftarrows AcONO + HOY ;$$
$$AcONO \rightleftarrows NO^{\oplus}AcO^{\ominus} ;$$
$$Y=H, Ac .$$

The unexpectedly high activity of nitrosonium acetate in the diazotisation reaction has been noted[15].

III. METHODS OF SYNTHESIS OF DIAZONIUM SALTS

Weakly basic aromatic and heterocyclic amines are usually diazotised in concentrated sulphuric acid, a mixture of sulphuric and phosphoric acids, a mixture of sulphuric and acetic acids, and also in concentrated nitric acid.

1. Diazotisation in Concentrated Sulphuric Acid

Diazotisation in concentrated sulphuric acid is suitable only for weakly basic amines. Aromatic amines with a high basicity are either precipitated from sulphuric acid in the form of salts (for example, aniline[16]) or are nitrosated in the *p*-position in the ring (for example, α-naphthylamine, *m*-toluidine, and *m*-anisidine[1]).

The diazotisation is as a rule carried out in the following manner. The amine is added with stirring and cooling to a solution of nitrosylsulphuric acid in sulphuric acid, prepared by the method of Fierz-David and Blangley[17], and the reaction mixture is then allowed to stand for the required time. The diazonium salt is either precipitated with ether or is made to undergo further reactions in concentrated sulphuric acid.

The time required for the complete diazotisation depends on the structure of the amine. Table 1 presents data on the diazotisation of weakly basic amines in concentrated sulphuric acid.

Table 1. Diazotisation of amines in sulphuric acid.

Amine	τ*, h	Refs.
3-Amino-2-carboxypyrazole	0.25	[4]
2,3,4,5-Tetrachloroaniline	1	[18]
2,3,5,6-Tetrachloroaniline	1	[18]
2,4,5-Trichloroaniline	1	[18]
2,3,4-Trichloroaniline	1	[18]
4-Fluoro-2-nitroaniline	1	[19]
2,4-Dinitroaniline	3	[17]
5-Chloro-2,4-dinitroaniline	4	[20, 21]
2,3,4,5-Tetrachloroanthranilic acid	16	[22]
4-Amino-2-iodoquinoline	—	[23]
p-Phenylenediamine	—	[24]**
2-Methyl-3,5-dinitroaniline	—	[25]

* Total diazotisation time.
** A bisdiazonium salt is formed.

The rate of diazotisation can be increased by diluting sulphuric acid with water[1]. However, this procedure is limited by the solubility of amines[21] and also by the decomposition of certain diazonium salts, for example 2,4,6-trinitrobenzenediazonium sulphate[3].

It has been noted[26] that the diazotisation of nitroanilines in concentrated sulphuric acid requires certain precautions: the reaction mixtures are very explosive in the case of dinitroanilines.

2. Diazotisation in a Mixture of Sulphuric and Acetic Acids

Weakly basic amines are diazotised successfully and at a high rate in a mixture of sulphuric and acetic acids. There are two methods, developed by Hodgson and co-workers, whereby the reaction can be carried out, depending on the solubility of the amine in acetic acid.

A. When the amine is soluble in acetic acid, its solution is added to the sulphuric acid solution of nitrosylsulphuric acid and care is taken to avoid the formation of a precipitate of the amine sulphate[27,28]. For example, *o*-phenylenediamine[27] and 4-nitro-1-naphthylamine[29] are diazotised in this way.

B. If the amine is sparingly soluble in acetic acid, it is recommended that it be initially dissolved in the sulphuric acid solution of nitrosylsulphuric acid and that an approximately equal amount of acetic acid is then added, as in the diazotisation of 1,6-dinitro-2-naphthylamine[30] or *p*-aminobenzaldehyde[31].

A list of weakly basic aromatic and heterocyclic amines, diazotised by the first and second methods in a mixture of sulphuric and acetic acids, is given in Table 2.

The method of diazotisation in acetic acid is used quite widely; it makes it possible to diazotise successfully not only weakly basic but also strongly basic aromatic and heterocyclic amines, provided that they do not decompose in sulphuric acid.

Table 2. Diazotisation of amines in a mixture of sulphuric and acetic acids.

Amine	Method	Refs.
3,5-Dibromo-1-nitroaniline	A	[32]
2,4-Diaminoquinoline	B	[23]
4-Amino-2-methoxyquinoline	B	[23]
o-Nitroaniline	A	[33]
m-Nitroaniline	A	[33]
p-Nitroaniline	A	[33]
2,4-Dinitronaphthylamine	A, B	[34, 35]
2,5-Dichloroaniline	A	[33]
3,5-Dinitro-*p*-toluidine	A	[33]
4-Trifluoromethyl-2-nitroaniline	A	[19]
4-Amino-2-nitrobenzaldehyde	A	[19]
4,5-Dinitronaphthylamine	A	[36]
4,4'-Diamino-3,3'-dinitrobiphenyl	B	[27]
2,3-Dinitroaniline	A	[37]
2,4,6-Tribromoaniline	A	[38]
p-Aminobenzaldehyde	B	[31]
2-Aminobenzo-1,4-dioxane	B	[39]
4-t-Butyl-1-nitroaniline	A	[40]

Diazonium sulphates can be isolated in the solid state by precipitation with ether or by other suitable solvents[41-43].

The relatively high freezing point of acetic acid, even in solution in sulphuric acid, must be regarded as a disadvantage of this method. If it is necessary to carry out the reaction at a low temperature, a mixture of acetic and propionic acid is used, for example, in the diazotisation of ethyl 5-aminothiophen-2-carboxylate[44].

3. Diazotisation in a Mixture of Sulphuric and Phosphoric Acid

The method of diazotisation in a mixture of sulphuric and phosphoric acids was developed by Schoutissen for weakly basic aromatic amines and diamines[16,31,35,45]. Diazotisation in a mixture of sulphuric and phosphoric acid takes place much more rapidly than in sulphuric acid alone. As in a mixture of sulphuric and acetic acids, the reaction is carried out by two methods: (1) a solution of the amine in sulphuric acid is added to a solution of nitrosylsulphuric acid in sulphuric acid; (2) phosphoric acid is added to a solution of the amine and nitrosylsulphuric acid in sulphuric acid.

Table 3 gives a list of the weakly basic aromatic and heterocyclic amines which have been diazotised by this method. The advantages of the method include the possibility of working at low temperatures.

Table 3. Diazotisation of amines in a mixture of sulphuric and phosphoric acids.

Amine	Refs.
2,4-Dinitroaniline	[16]
2,4,6-Trinitroaniline*	[16]
1,4-Diamino-2,5-dichlorobenzene**	[16]
o-Phenylenediamine**	[8]
p-Aminobenzaldehyde	[31]
2-Amino-1,3-selenazole	[46]
2-Amino-4-phenyl-1,3-selenazole	[46]
2,3-Dinitroaniline	[47]
2,6-Dinitroaniline	[47]
2,4-Difluoro-5-nitroaniline	[48]
2,6-Di-iodo-4-nitroaniline	[49]

* 2,4,6-Trinitroaniline is first dissolved in nitrobenzene.
** Bisdiazonium salts are formed.

4. Diazotisation in Concentrated Nitric Acid

It has been shown[50,51] that certain amines can be smoothly diazotised in concentrated nitric acid. The reaction takes place much faster than in concentrated sulphuric acid and is actually faster than in mixtures of sulphuric acid with acetic or phosphoric acid. The diazotisation frequently reaches completion after several minutes, which can be explained by the high solvent power of concentrated nitric acid.

Despite these advantages, the method is used rarely, because there is a risk that part of the amine is nitrated before being diazotised[52,53].

The reaction in nitric acid is carried out using different diazotising agents. Thus 2,6-nitro-4-toluidine is diazotised by nitrous oxides[50]; 4-amino-3,5-dibromobenzoic acid is diazotised with potassium nitrite[54]; 3,4,5-tri-iodoaniline is diazotised with sodium nitrite[55]; 2-methyl-3,5-dinitroaniline[25] and 13-aminobenzanthrone[56] are diazotised with nitrosylsulphuric acid formed when potassium thiosulphate is introduced into nitric acid. It is noteworthy that the diazotised amine is nitrated very slowly[56] owing to the powerful negative mesomeric effect of the diazo-group[57].

5. Diazotisation in Organic Solvents

This method is used fairly rarely for weakly basic amines. Thus 6-bromo-2,4-dinitroaniline[2] is diazotised by a mixture of nitrosylsulphuric and formic acids in tetrahydrothiophen 1,1-dioxide, while 2,4,6-trinitroaniline[16] is diazotised by a mixture of nitrosylsulphuric and phosphoric acids in nitrobenzene.

It has been reported[58] that 2,4,6-trinitroaniline can be smoothly diazotised by nitrosylsulphuric acid in a mixture of pyridine and sulphuric acid and the product of the azo-coupling of the diazonium salt with β-naphthol was actually isolated. Later, when an attempt was made to confirm this investigation, it was established[59] that diazotisation does not take place in this instance and that the so-called "product of the azo-coupling reaction" is an equimolar adduct of β-naphthol and picramide.

The attempt to obtain diazonium salts from 2,4,6-trichloro- and 2,4,6-tribromoanilines with the aid of nitrosylsulphuric acid in ethanol[18] should also be mentioned: after the decomposition of the reaction mass, only the corresponding diaryltriazenes were isolated, which indicates a low rate of diazotisation.

The question of the limits of the applicability of the reaction is obscure and the possibility of the diazotisation of weakly basic amines in organic solvents must be elucidated in each individual instance.

Thus weakly basic aromatic and heterocyclic amines can be most conveniently diazotised by nitrosylsulphuric acid in a mixture of concentrated sulphuric and phosphoric ($d = 1.7$) or acetic acids. Phosphoric acid mixtures make it possible to carry out the reaction at a low temperature. Other diazotising mixtures are rarely employed.

IV. REACTIONS OF DIAZONIUM SALTS

The reactions of diazonium ions have been investigated for a very long time. Various reactions of diazonium salts, leading to compounds which cannot be obtained by other methods, are known.

There exist several classifications of the reactions of diazonium ions. The most complete modern classification was devised by Zollinger[60] in 1973.

The present review deals only with those reactions which are known for diazonium salts obtained from weakly basic aromatic and heterocyclic amines by diazotisation in strongly acid media. They are frequently divided into three types:

1. Reactions involving addition to the β-atom of the diazo-group (azo-coupling with electron-donating π-electron systems, the formation of triazenes and azido-derivatives);
2. reactions with heterolytic dissociation of the bond between the ring carbon atom and a nitrogen atom of the diazo-group (hydrolysis);
3. reactions with homolytic dissociation of the same bond (substitution by halogen-, nitro-, and cyano-groups and reduction of diazonium salts).

1. Azo-Coupling with π-Electron Systems

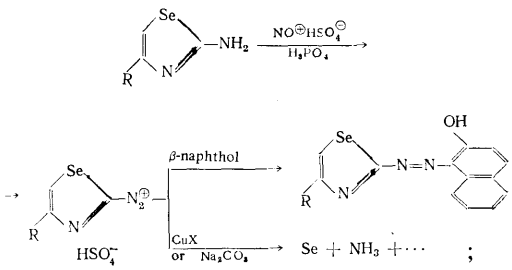
One of the most characteristic reactions of diazonium salts is that of azo-coupling. The azo-coupling reaction is usually carried out in nearly neutral media, because in an acid medium the amines and the phenols employed as the azo-components are protonated and to a large extent lose their activity.

The reaction is accelerated when the arenediazonium cation contains one or several electron-accepting groups. Thus the 2,4,6-trinitrobenzenediazonium ion reacts even with a relatively inactive azo-component such as mesitylene[61].

When the diazonium salts are difficult or impossible to obtain in the solid state or in an aqueous solution of moderate acidity, their azo-coupling is carried out in strongly acid

solutions by adding the azo-component in the solid state or in solution in pyridine[16] or methylene chloride[62]. β-Naphthol or phenol are usually employed as the azo-component. The precipitate of the azo-coupling product is usually bright red.

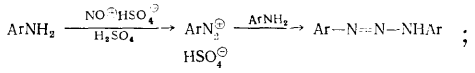
Among the chemical methods, this reaction constitutes the most reliable procedure for the detection of diazonium salts. In many cases the presence of diazonium salts is tested by the azo-coupling reaction. Thus the formation of diazonium salts in the diazotisation of 2-amino-1,3-selenazoles by a mixture of nitrosylsulphuric and phosphoric acids was confirmed solely by the reaction with β-naphthol, while the interaction with other reagents leads only to decomposition products[43]:



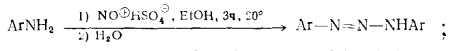
R=H, Ph .

2. The Formation of Triazenes

Triazenes are usually formed on diazotisation of amines (particularly weakly basic amines) in a weakly acid medium. The use of strong acids, prevents this reaction. If the diazotisation has not been carried out to completion or additional amine is introduced into the reaction mass which has fully reacted, there is a possibility of the formation of 1,3-disubstituted triazenes when the strongly acid solutions are poured into water[18]:

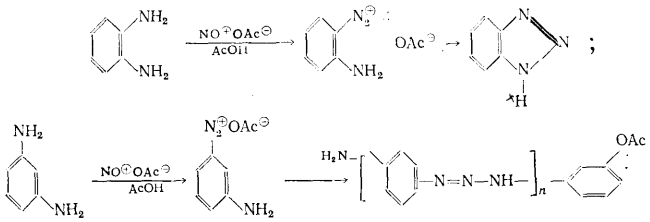


$ArNH_2$ = 2,4,6-trichloro- or 2,4,6-tribromo-aniline;



$ArNH_2$ = 1,2,4,5-tetrachloro-, 2,3,4,6-tetrachloro-, 2,4,5-trichloro-aniline, etc.

It is particularly important to take this reaction into account in the decomposition of monodiazonium salts obtained from diamines. This entails the formation of both cyclic (from *o*-phenylenediamines) and linear triazenes[7,63]:

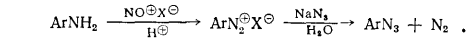


3. The Formation of Azido-Derivatives

Diazonium salts interact with ammonia, hydrazine and many of their derivatives, such as hydroxylamine, arenesulphonamides, phenylhydrazine, and aromatic acid hydrazides with formation of azides.

However, these methods are applicable to weakly basic or neutral solutions of diazonium salts, because in strong acids ammonia and hydrazine derivatives are protonated and do not react with diazonium cations.

For weakly basic amines, the most common reaction of diazonium salts is that with hydrazoic acid and its salt. The yields of azidoarenes are high, frequently nearly quantitative:



For example, 1-azido-4-trifluoromethyl-2-nitrobenzene, 1-azido-4-formyl-2-nitrobenzene, 1-azido-4-fluoro-2-nitrobenzene[19], and 1-azido-4,6-dibromo-2-nitrobenzene[32] are obtained in this way.

In the case of 2,2′-diaminoazobenzene and 2,4,6-triaminomesitylene it is possible to introduce two[64] or three[65] azido-groups respectively.

4. Substitution by the Hydroxy-Group

Virtually all diazonium salts react with water, exchanging the diazo-group for a hydroxyl. For diazonium salts obtained from weakly basic amines, this reaction can actually interfere with its normal reactions and can compete with the reaction involving substitution under the influence of other nucleophiles[3,4].

Strongly acid solutions of diazonium salts obtained from weakly basic amines are decomposed by being poured into water, as in the case of 3-carboxypyrazole-2-diazonium sulphate[4], or into a solution of copper sulphate, as in the case of 2,3,4,5-tetrachlorobenzenediazonium sulphate[22]. When necessary, dilute solutions of diazonium salts are refluxed. For example, *p*-hydroxybenzaldehyde[31] and 2- and 4-hydroxyquinolines[23] are obtained in this way.

5. Substitution by the Chloro-, Bromo-, Nitro-, and Cyano-Groups (The Sandmeyer Reaction)

When a solution of a diazonium salt is treated with an appropriate nucleophile X^- (X = Cl, Br, NO_2, or CN) in the presence of a copper catalyst, the diazo-group is replaced by the chloro-, bromo-, cyano-, or nitro-group. The catalyst can consist of metallic copper, copper(I) oxide, copper(II) oxide, or copper(II) sulphate as well as copper(I) salts (the chloride, bromide, and cyanide).

The Sandmeyer reaction is carried out as a rule in a neutral or weakly acid medium. The diazonium salts obtained from weakly basic amines by diazotisation in strongly acid media are also decomposed by being poured into a solution of the corresponding nucleophile in the presence of the copper catalyst.

The substitution by chlorine (or bromine) is usually carried out by adding a solution of copper(I) chloride (bromide) in hydrochloric (hydrobromic) acid to a solution of the diazonium salt.

Nitro-compounds are best obtained with preliminary precipitation of the diazonium salt from strongly acid solutions with ether.

The reaction involving the substitution of the diazo-group by the cyano-group is rarely used. It is usually carried out in a rigorously neutral medium by adding a solution of an alkali metal cyanide and copper sulphate (copper monocyanide is sometimes used). For example, *o*-, *m*-, and *p*-nitroanilines[66], 3-aminopyridine, and 5-amino-2-methylpyridine[67] are diazotised in this way.

Data for the Sandmeyer reaction of hydrochloric acid solutions of diazonium salts are presented in Table 4.

The Sandmeyer reaction does not occur when the competing hydrolytic reaction proceeds at a higher rate, as for 2-carboxypyrazolediazonium sulphate[4], or when the heterocycle is ruptured[46].

Table 4. The Sandmeyer reaction for weakly basic aromatic and heterocyclic amines.

Amine	Diazotising mixture	Substituting anion	Decompn. mixture	Refs.
2,3-Dinitroaniline	$NOHSO_4+H_3PO_4$	$Cl^{\ominus}$	HCl+CuCl	[47]
ditto	$NOHSO_4$+AcOH	$Br^{\ominus}$	HBr+CuBr	[37]
2,6-Dinitroaniline	$NOHSO_4+H_3PO_4$	$Cl^{\ominus}$	HCl+CuCl	[47]
4,5-Dinitronaphthylamine	$NOHSO_4$+AcOH	$Cl^{\ominus}$	ditto	[36]
ditto	ditto	$Br^{\ominus}$	HBr+CuBr	[36]
4,4'-Diamino-3,3'-dinitrobiphenyl	»	$Cl^{\ominus}$	HCl+CuCl	[27]
2,4-Dinitronaphthylamine	»	$Cl^{\ominus}$	ditto	[27]
ditto	»	$Br^{\ominus}$	HBr+CuBr	[27]
4-Amino-2-methoxyquinoline	»	$Cl^{\ominus}$	HCl+CuCl	[23]
ditto	»	$NO_2^{\ominus}$	$NaNO_2+Cu_2O$	[23]
2,4-Diaminoquinoline	»	$Cl^{\ominus}$	HCl+CuCl	[23]
ditto	»	$NO_2^{\ominus}$	$NaNO_2+Cu_2O$	[23]
4-Bromo-2,6-dinitroaniline	$NOHSO_4$	$Br^{\ominus}$	HBr+CuBr	[68]
2-Amino-3,4,5,6-tetrachlorobenzoic acid	ditto	$Br^{\ominus}$	ditto	[69]
4-Amino-3-nitroanisole	»	$Br^{\ominus}$	»	[70]
2,4,6-Tribromoaniline	$NOHSO_4$+AcOH	$Br^{\ominus}$	»	[38]
p-Phenylenediamine	ditto	$CN^{\ominus}$	KCN+CuCN	[66]
m-Phenylenediamine	$NOHSO_4$+AcOH	$CN^{\ominus}$	»	[66]
3,5-Dinitronaphthylamine	ditto	$NO_2^{\ominus}$	$NaNO_2+CuSO_3$	[71]
7-Amino-6-nitrotetralin	»	$NO_2^{\ominus}$	»	[71]

Table 5. Substitution of the diazo-group by iodine in diazonium salts obtained in a strongly acid medium.

Amine	Diazotising mixture	Refs.
2-Amino-4,5-dinitrobenzoic acid	$NOHSO_4+H_2SO_4$	[72]
2,4-Difluoro-6-nitroaniline	$NOHSO_4+H_3PO_4$	[48]
2,6-Di-iodo-4-nitroaniline	ditto	[49]
4-Amino-3,5-dibromobenzoic acid	$NOHSO_4+H_2SO_4$	[73]
2,3-Dinitroaniline	$NOHSO_4$+AcOH	[37]
p-Aminobenzaldehyde	$NOHSO_4+H_3PO_4$(AcOH)	[31]
2-Aminobenzo-1,4-dioxan	$NOHSO_4$+AcOH	[39]
4-Amino-2-methoxyquinoline	ditto	[23]
2,4-Diaminoquinoline	»	[23]
2,4-Dinitro-1-naphthylamine	»	[74]
1,6-Dinitro-2-naphthylamine	»	[74]

6. Substitution by Iodine

The substitution of the diazo-group by iodine does not require the presence of copper catalysts. It takes place when strongly acid solutions of diazonium salts are poured into a solution of potassium iodide. A list of weakly basic amines which have been made to undergo this reaction is presented in Table 5.

7. Substitution by Hydrogen (Reduction)

Diazonium salts can be reduced with the aid of many reagents. The most common are alcohol and hypophosphorous acid. (In relation to the initial amine, this reaction is referred to as deamination.)

Diazonium salts obtained from weakly basic amines such as 2,4-dinitrotoluidine[50] and 5-t-butyl-2-nitroaniline[40] are usually reduced by heating with ethanol. Copper catalysts are sometimes used, for example, copper(II) oxide for *o*-, *m*-, and *p*-nitroanilines, 2,4-dinitronaphthylamine, and 2,5-dichloroaniline[33] or copper sulphate for 2,6-dibromo-4-carboxyaniline[54].

2,4,6-Trinitroaniline can be conveniently deaminated with hypophosphorous acid[75].

Summarising the above discussion, one may say that the diazonium salts obtained from weakly basic amines in strongly acid media are capable of undergoing various reactions both with and without the evolution of molecular nitrogen. The reactions without the evolution of a nitrogen molecule (azo-coupling and the formation of triazenes) as a rule take place readily. The methods for the substitution of the diazo-group by various functional groups have been developed less fully owing to the low stability of the diazonium salts in aqueous media.

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Three-membered Organophosphorus Heterocycles

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The methods of synthesis, structural characteristics, and properties of compounds with three-membered rings and containing at least one phosphorus atom and one carbon atom, including bicyclic and tricyclic compounds, are examined. The bibliography includes 76 references.

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I. INTRODUCTION

Three-membered rings occupy a special position in theoretical and applied organic chemistry as a consequence of characteristic features of orbital hybridisation, the high angular strain, and the consequent ease of ring opening or expansion. The introduction of a heteroatom into a three-membered ring lowers the molecular symmetry and results in the non-equivalence of the angles and bonds, expressed to the greatest extent in the case of a ring containing a phosphorus atom.

It is noteworthy that compounds with three-membered phosphorus-containing heterocycles (phosphirans) have been studied comparatively little, since they have been obtained only very recently. In the monograph of Kirby and Warren[1], the English edition of which was published in 1967, it is still stated that "stable three-membered rings containing phosphorus are unknown except for the elemental phosphorus P_4. However, they can arise as intermediates or in transiton states...".[2,3] The intermediate formation of unstable compounds with a three-membered phosphorus-containing ring was invoked to account for the mechanism of formation of reaction products and has also been postulated in a number of other studies[4-10], while the synthesis of relatively stable phosphirans and element-substituted phosphirans as well as the study of their properties have been described as a rule only during the last decade.

Baudler's review[11], devoted to compounds with three-membered rings consisting solely of phosphorus atoms, or of two phosphorus atoms and a single carbon, silicon, germanium, arsenic, boron, or sulphur atom, or of two arsenic atoms and a single phosphorus atom, i.e. in most cases referring to inorganic rings, was published in 1980. The present review deals solely with three-membered phosphorus-containing rings with at least one carbon atom, so that the data presented constitute an organic supplement to Baudler's review[11].

Data on the synthesis and NMR spectra of phosphirans containing only phosphorus and carbon atoms are also considered in Quin's monograph[12] devoted to P-C heterocycles.

II. SYNTHESIS

1. Rings with Tetracoordinate Phosphorus

The simplest compound, the unsubstituted phosphiran, was the first to be synthesised among compounds containing a three-membered heterocycle with a phosphorus atom and a P-C bond. In their study of the reaction of α,ω-dihalogenoalkanes with alkali metal phosphides in liquid ammonia, which was undertaken with the aim of synthesising α,ω-diphosphinoalkanes, Wagner and co-workers[13,14] unexpectedly observed that, when 1,2-dichloroethane is used, the product is phosphiran or 1-methylphosphiran. According to Wagner et al.[14], this course of the reaction can be explained by the fact that the hydrogen linked to the phosphorus atom in the intermediate formed on substitution of the first chlorine atom in dichloroethane readily exchanges for the metal on treatment with sodium phosphide or methylphosphide, which then leads to cyclic products:

$$ClCH_2CH_2Cl \xrightarrow[-Cl^-]{RPH^-} ClCH_2CH_2PHR \xrightarrow[-RPH_2]{RPH^-} \rightarrow ClCH_2CH_2\bar{P}R \xrightarrow[-Cl^-]{} \underset{\diagdown P \diagup}{CH_2—CH_2} \; ;$$

$$\underset{R}{|}$$

R=H, Me .

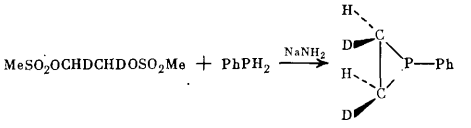
Wagner's method proved to be of general validity for the synthesis of C- and P-substituted phosphirans. The use of other 1,2-dichloroalkanes and monosubstituted sodium phosphides in this reaction made it possible to obtain a series of 1-alkyl(aryl)- and 2-alkyl-phosphirans in yields of 25-60%.[15] According to ^1H NMR data, 2-alkylphosphirans are then obtained in the form of a mixture of *cis*- and *trans*-isomers. In order to investigate the properties of phosphirans and to establish their structural characteristics (see Section III), various isotope-substituted phosphirans were synthesised. Thus the interaction of sodium dideuterophosphide with dichloroethane in liquid trideuteroammonia[16] or hexamethylphosphoramide[15,17] led to 1-deuterophosphiran; 2-deuterophosphiran[15,17], 2,2,3,3-tetradeuterophosphiran[16] and [^{13}C]phosphiran[15,17] were synthesised analogously by the reaction of monodeuterodichloroethane, perdeuterodichloroethane, and [^{13}C]dichloroethane respectively with sodium phosphide in liquid ammonia. The phosphirans were isolated by fractional vacuum condensation. The structures of the products were determined from infrared spectroscopic, ^1H and ^{31}P NMR, and mass-spectrometric data, and also from ebullioscopic determinations of their molecular weights.

An unusual version of the reaction described above involves the interaction of 2-bromoethyldibromophosphine with lithium tetrahydroaluminate in the diethyl ether of diethylene glycol. Evidently the initial products in this case are the corresponding phosphine, which then cyclises intramolecularly to a three-membered ring[14]. Apart from the phosphiran, ethylphosphine, phosphine, and ethylene are formed under these conditions:

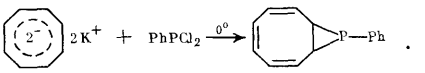
$$BrCH_2CH_2PBr_2 \xrightarrow{LiAlH_4} \underset{\diagdown P \diagup}{CH_2—CH_2} + EtPH_2 + C_2H_4 + PH_3 \; .$$

$$\underset{H}{|}$$

The cyclisation of 1,2-disubstituted ethanes can take place not only as a result of the elimination of the halogen from the carbon atom, the methanesulphonyloxy-substituent also being capable of functioning as the leaving group. For example, in the presence of sodium amide, phenylphosphine interacts with 1,2-dideutero-1,2-bis(methanesulphonyloxy)ethane to form *cis*-2,3-dideutero-1-phenylphosphiran[18]:

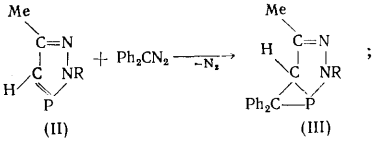


When readily eliminated halogen atoms are present at the phosphorus atom, the phosphorus compound can be involved in the synthesis of phosphirans as an electrophile. Thus 9-phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene (I) has been obtained by the condensation of the dipotassium salt of cyclo-octatetraene with dichlorophenylphosphine under mild conditions[19,20]:



(I)

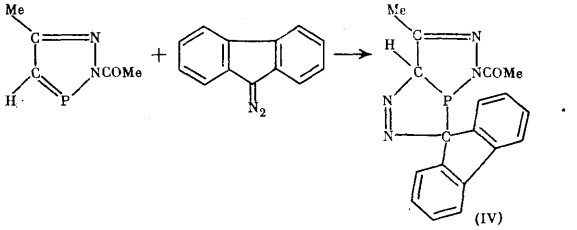
Arbuzov and co-workers recently described a method for the formation of the phosphiran ring with a tervalent phosphorus atom, which consists in the addition of diphenyldiazomethane to the P=C bond in compounds with dicoordinate phosphorus[21,22]. In this case the phosphorus atom is shared by two rings. The products are crystalline substances (III) with high melting points and some of the highest thermal stabilities among compounds with a phosphiran ring. Their structure has been confirmed by infrared spectroscopy and ^{1}H and ^{31}P NMR, by determining their molecular weights, and by a series of reactions:



(II) (III)

R=Ph, MeCO .

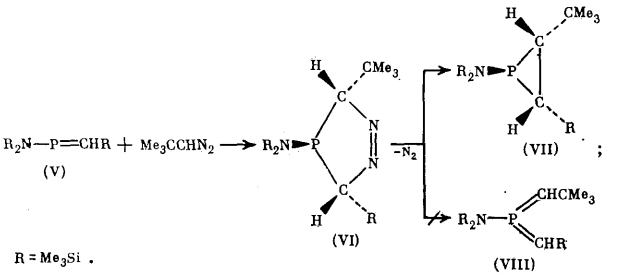
Despite the conditions being varied, products containing the phosphiran ring are not formed in the analogous interaction of the diazaphosphole (II, R=MeCO) with 9-diazofluorene. However, when the reaction is carried out in pentane or hexane, the adduct (IV) is produced in almost quantitative yield, its formation suggesting that diazoalkanes add to the P=C bond in diazaphospholes (II) via the 1,3-cycloaddition mechanism and not via a carbene[23]:



(IV)

The interaction of 2,2-dimethyldiazopropane with a noncyclic derivative of dicoordinate phosphorus (V) also leads to a stable 1,3-cycloaddition product, namely 3-trimethylsilyl-4-[bis(trimethylsilyl)amino]-5-t-butyl-1,2,4λ^3-diazaphospholine (VI). However, on heating *in vacuo* at temperatures between 80° and 120 °C, the diazaphospholine (VI) splits off nitrogen and gives rise to the corresponding phosphiran (VIII), whose configuration has been postulated on the basis of spectroscopic data.

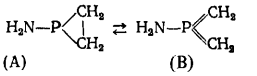
The possibility of the formation of aminodimethylenephosphine (VIII) has also been postulated in the decomposition of the diazaphospholine (VI).



(V) (VI) (VII) (VIII)

R = Me_3Si .

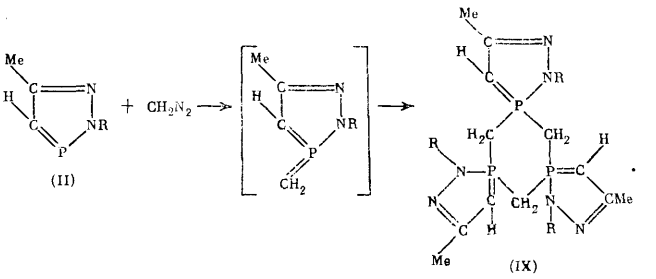
However, calculation of the energy surface for the valence isomerisation of the model structure



(A) (B)

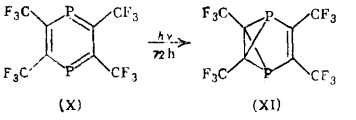
by the MINDO/3 method showed that the cyclic form (A) is more favourable by 22 kcal $mole^{-1}$ than the dimethylenephosphine form (B) and that the A⇌B transition has a comparatively high energy barrier[24].

A similar dimethylenephosphino-derivative, analogous to compound (VIII), is apparently formed as an intermediate in the reaction of 1,2,3-diazaphospholes with diazomethane, since the products are not phosphirans but three-dimensional compounds (IX):



(II) (IX)

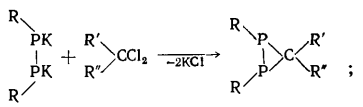
When 2,3,5,6-tetrakis(trifluoromethyl)1,4-diphosphabenzene (X) is illuminated for a long time, the product is a tricyclic compound containing two phosphiran rings with tervalent phosphorus—2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphatricyclo[3.1.0.$0^{4,6}$]hex-2-ene (XI). This compound is the first representative of the analogues of benzvalene with heteroatoms in the ring[25-27]:



(X) (XI)

Three-membered rings with two phosphorus atoms, namely diphosphirans (XII), were obtained for the first time by the reaction of the dipotassium salts of symmetrical dialkyl(aryl)-diphosphines with geminal dichloroalkanes in pentane or toluene at −30 °C.[11,28,29]. Their formation reaction can be regarded as an unusual version of the Wagner synthesis of

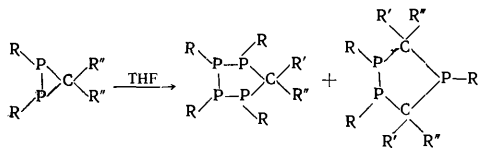
phosphirans, since in this case too the halogen at the saturated carbon atom undergoes nucleophilic substitution by the phosphide anion:



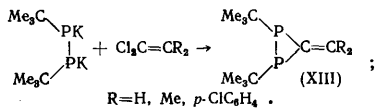
(XII)

R = t-Bu, R′, R″=H, Me; R=Ph, R′, R″=Me .

It is of interest that, when this reaction is carried out in tetrahydrofuran (THF), five-membered and not three-membered phosphorus-containing heterocycles are produced[29], which has been explained by a rapid rearrangement of the diphosphirans in the more polar solvent[11]:



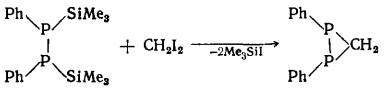
Diphosphirans (XIII) having an exocyclic C=C bond have been obtained by the reaction of 1,2-di-t-butyl-1,2-dipotassio-diphosphine with 1,1-dichloro-olefines as well as geminal dichloroalkanes[11]:



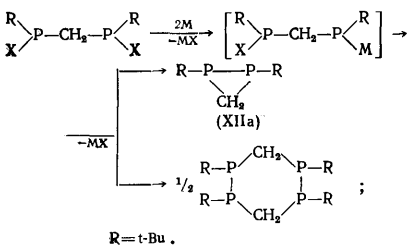
(XIII)

R=H, Me, *p*-ClC$_6$H$_4$.

The reaction of 1,2-bis(trimethylsilyl)-1,2-diphenyldiphopshine with di-iodomethane in THF at −30°C apparently also leads to 1,2-diphenyldiphosphiran[28], since a signal in the appropriate region appears in the ^{31}P NMR spectrum:

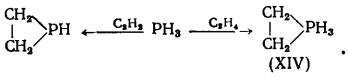


1,2-Di-t-butyldiphosphiran (XIIa) has also been obtained by the intramolecular 1,3-cyclisation of the corresponding *P,P*-dihalogenodiphosphinomethane by treatment with a liquid potassium–sodium alloy at temperatures between 0° and 10 °C (yet another version of the Wagner reaction). Diphosphiran is then obtained in the form of a mixture with a dimer—1,2,-4,5-tetra-t-butyl-1,2,4,5-tetraphosphacyclohexane—and constitutes 80% of the mixture. The diphosphiran could not be detected in the analogous reaction of *P,P*-dihalogenodiphosphinomethane with isopropyl groups at the phosphorus atoms—the corresponding tetraphosphacyclohexane is formed immediately[30]:



R=t-Bu .

Thus the most general methods of synthesis of phosphirans with tervalent phosphorus are different versions of the interactions of alkali metal phosphides with compounds containing two readily removed groups (a halogen or the methanesulphonyloxy-group) in the 1,2- or 1,1-positions and also the addition of diazoalkanes to compounds of dicoordinate phosphorus, which has also been used to synthesise phosphirans with tetracoordinate phosphorus and with a nitrogen atom in the phosphiran ring (see below). Other syntheses known at present have been described only in relation to individual examples. The theoretical possibility of yet another method of synthesis of unsubstituted phosphirans as well as the synthesis of a phosphiran with a pentacoordinate phosphorus atom [structure (XIV)] as a result of the addition of phosphine to acetylene and ethylene respectively has been predicted on the basis of the analysis of Woodward–Hoffman correlation diagrams:

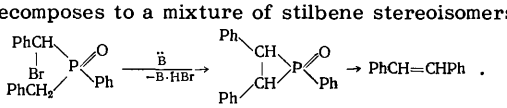


(XIV)

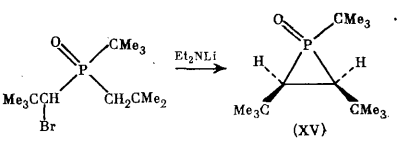
The authors believe that the first reaction can occur in the ground state, while the second takes place on photochemical oxidation of the molecules and also under the conditions of acid and base catalysis. Substitution of the hydrogen atoms in the phosphine by more electronegative groups should impair the energetics of the formation of the phosphiran ring[31]. However, hitherto this synthesis has not been realised.

2. Rings with Tetracoordinate Phosphorus

Only one method of synthesis of phosphiran oxides has been described so far. It involves the 1,3-cyclisation under the influence of a base of acyclic oxides containing a halogen atom in the α-position in one of the substituents at the phosphorus atom and a mobile hydrogen atom in the α-position in the other substituent. Thus 1,3-elimination of hydrogen halide from α-bromobenzylphenylbenzylphosphine oxide results in the formation of 1,2,3-triphenylphosphiran oxide, which decomposes to a mixture of stilbene stereoisomers[32]:

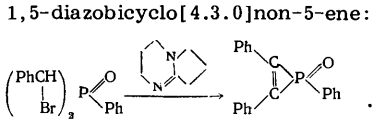


A stable phosphiran oxide (XV) with the *cis*-configuration and containing three t-butyl groups has been obtained recently as a result of an analogous cyclisation[33,34]. The configuration of the product has been proposed on the basis of ^{1}H and ^{13}C NMR data:



(XV)

It has been reported[32,35] that 1,2,3-triphenylphosphiran oxide (XVI) has been obtained as a result of the analogous cyclisation of bis(α-bromobenzyl)phenylphosphine oxide on treatment with 1,5-diazobicyclo[4.3.0]non-5-ene:



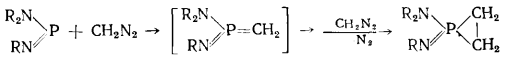
(XVI)

However, the formation of this phosphiran oxide has been refuted[36] on the basis of the physical and spectroscopic characteristics of the product obtained on repeating the above reaction, although one should note that the infrared and mass spectra of the compounds synthesised by the two groups of investigators are different.

Nevertheless the possibility, in principle, of the existence of compounds with a phosphiren ring forming an aromatic system as a consequence of delocalisation of the $p\pi$ electrons of the double bonds via $p_\pi - d_\pi$ conjugation, has been considered in a study[37] whose authors concluded that fairly stable phosphirenium salts and phosphiren oxides (analogues of cyclopropenone) exist:



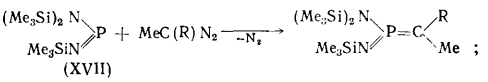
Like the analogous compounds with the C = P–N group (see above), compounds of dicoordinate phosphorus with the N = P–N group are capable of reacting with diazoalkanes although via a somewhat different mechanism. For example, the addition of diazomethane to bis(trimethylsilyl)aminotrimethylsilyliminophosphine (XVII) leads to 1-bis(trimethylsilyl)amino-1-trimethylsilyliminophosphiran (XVII)—a representative of phosphirans with an exocyclic phosphazo-group[38]:



(XVII) (XVIII) ;

R = Me_3Si .

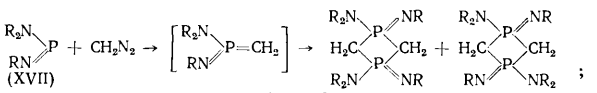
The intermediate formation of an ylide with a tricoordinate phosphorus atom is confirmed by the fact that the reaction of the aminoiminophosphine (XVII) with other diazoalkanes stops at the ylide stage. The ylides are stable for steric reasons, as suggested by Niecke and Wildredt[39]:



(XVII)

R = Me, Et, iso-Pr, t-Bu .

In addition, when the conditions of the reaction between the phosphine (XVII) and diazomethane are modified somewhat, a mixture of isomeric diphosphetans, which are cyclic dimers of the intermediate phosphazoylide, is formed[40]:

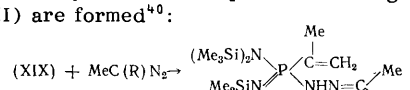


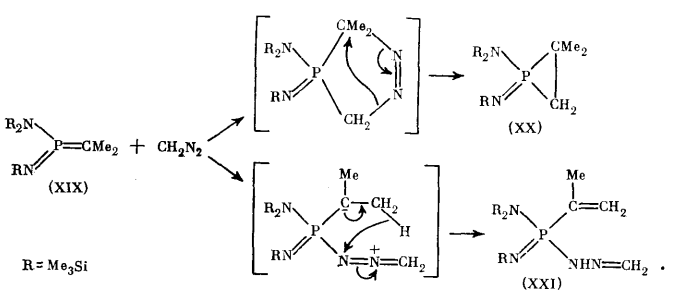
(XVII)

R = Me_3Si .

When diazomethane adds to the iminomethylenephosphine (XIX), the product is, as in the formation reaction of compound (XVIII), a compound (XX) with a phosphiran ring together with an acyclic compound (XXI) (in proportions of 7 : 3).[40]

The addition of α-alkyldiazoethanes to the iminoethylenephosphine (XIX) takes place, as in the case of compound (XVII), without cyclisation and products analogous to compound (XXI) are formed[40]:



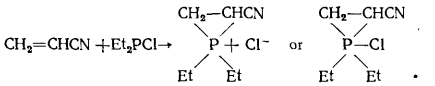


(XIX) (XX) (XXI)

R = Me_3Si .

3. Rings with Pentacoordinate Phosphorus

When chlorodiethylphosphine was made to add to acrylonitrile, a crystalline very hygroscopic substance was obtained. On the basis of infrared and ^1H NMR spectra as well as the study of its hydrolysis products, it was assumed to have the structure of 2-cyano-1,1-diethylphosphiranium or a derivative of pentacoordinate phosphorus—1-chloro-2-cyano-1,1-diethylphosphiran (XXII)[41]:



(XXII)

The formation of this compound is the only example of the 1,2-addition of a chlorophosphine to an activated olefinic bond. However, one should note that the interaction of chlorodiethylphosphine with acrylic and methacrylic acids and their chlorides also results in the formation of hygroscopic crystalline adducts. Whether these compounds are products of the 1,2-addition of the phosphine to the C = O bond is unknown, since their structure has not been investigated[42].

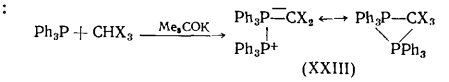
Even in the presence of antimony pentachloride, chlorodiphenylphosphine does not react with acrylonitrile[41].

The intermediate formation of compounds with pentacoordinate phosphorus containing a phosphiran ring is postulated in the reactions of 1-phenylphosphiran with 3,3,4-trimethyldioxetan and 3,4-bis(trifluoromethyl)dithietan[18,43] (see Section IV).

The products of the reactions of triorganylphosphines with ethoxyacetylene may contain a phosphiren ring with pentacoordinate phosphorus[7]:

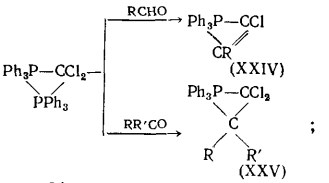


When triphenylphosphine reacted with chloroform or bromoform and potassium t-butoxide in proportions of 2 : 1 : 1, high-melting products (XXIII), having the structure of diphosphirans or betaines (XXIII), were obtained. The reaction of the chloro-compound (XXIII, X = Cl) with a series of aldehydes is accompanied by the elimination of a hydrogen chloride molecule and leads to products to which the structure of phosphirens (XXIV) was attributed. In the reactions involving benzophenone and 2-methoxybenzaldehyde, compounds (XXV) with a saturated phosphiran ring are obtained. Their structure has been postulated on the grounds that their infrared spectra contain absorption bands at frequencies characteristic of the three-membered phosphorus-containing ring[44–46]:



(XXIII)

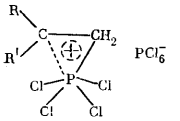
R = Ph, Pr, 2-MeC_6H_4, 2-HOC_6H_4, 2-$NO_3C_6H_4$, PhCH = CH



(XXIV) (XXV)

R, R′ = Ph; R = H, R′ = 2-$MeOC_6H_4$.

The structure of a three-centre epiphosphiran cation[47] of the type

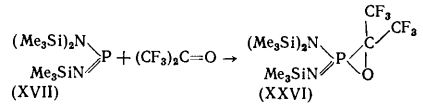


has been attributed to the transition state in the reactions of alkenes with phosphorus pentachloride.

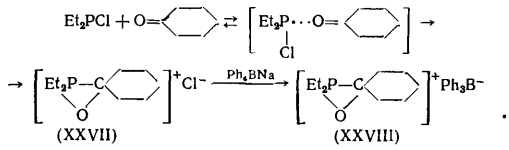
4. Element-substituted Phosphirans

Element-substituted phosphirans, whose three-membered ring contains, apart from phosphorus and carbon atoms, also oxygen, sulphur, or nitrogen atoms, are very few. The possibility of the intermediate formation of unstable compounds with an oxaphosphiran ring has been postulated in considering the mechanisms of reactions important in the chemistry of organophosphorus compounds such as that of trialkyl phosphites with α-diketones[8] or α-halogenoketones[9].

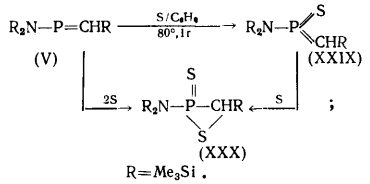
The first stable oxaphosphiran derivative (XXVI) was obtained only recently[48] as a result of the addition of hexafluoroacetone to the aminoiminophosphine (XVII). As in the reaction with diazomethane, only the phosphorus atom of (XVII) is involved in the reaction with hexafluoroacetone:



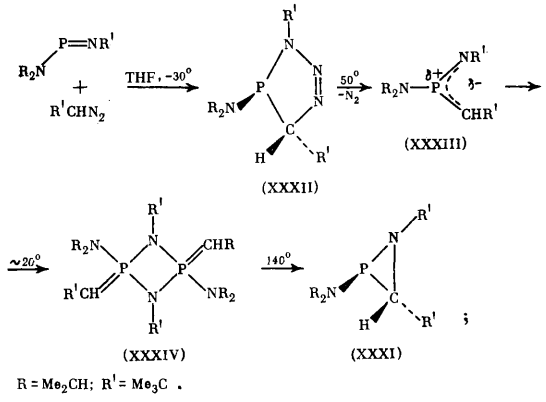
A crystalline compound, which is unstable in air and has the structure of a substituted oxaphosphiranium salt (XXVII), was isolated from the mixture of the products of the reaction of chlorodiethylphosphine with cyclohexanone. The more stable oxaphosphiranium salt (XXVIII) was obtained in the exchange of the anion of the chloride (XXVII)[49]:



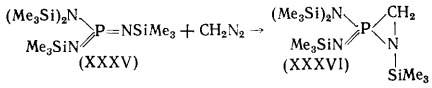
When an equivalent amount of sulphur adds to the aminomethylenephosphine (V), the corresponding sulphide (XXIX) is obtained together with a small amount of the thiaphosphiran (XXX), characterised by hydrogen, phosphorus, carbon, and silicon NMR data; the preferential formation of the sulphide (XXIX) shows that the thiaphosphiran ring is closed as the result of the addition of sulphur to the P=C bond of the sulphide and not the initial phosphine (V). The phosphine (V) reacts with two equivalents of sulphur to give a quantitative yield of the thiaphosphiran (XXX), which is the first representative of this heterocyclic system[50]:



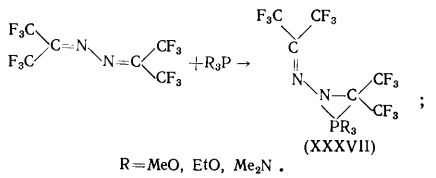
The interaction of t-butyliminodi-isopropylaminophosphine with 2,2-dimethyldiazopropane leads ultimately to 1,3-di-t-butyl-2-di-isopropylaminoazaphosphiridine (XXXI). The formation of compound (XXXI) completes the chain of transformations of the intermediates having structures (XXXII), (XXXIII), and (XXXIV), which were isolated in a pure state and characterised by ^{1}H, ^{13}C, and ^{31}P NMR data[51]:



In contrast to the P=N bond of the aminoiminophosphine (XVII) containing dicoordinate phosphorus, the analogous bond in the aminodi-iminophosphine (XXXV), containing tricoordinate phosphorus, is capable of the 1,2-addition reaction with diazomethane resulting in the formation of the azaphosphiridine (XXXVI), which is stable in the absence of moisture almost indefinitely[38]:



The addition of phosphorous acid derivatives to hexafluoroacetone azine takes place at only one C=N bond with formation of thermally stable azaphosphiridines (XXXVII) with a pentacoordinate phosphorus atom. Their structure has been postulated on the basis of infrared spectroscopic, ^{19}F and ^{13}C NMR and mass-spectrometric data[52]:



III. STRUCTURE AND PHYSICAL PROPERTIES

The structure of compounds with a three-membered ring containing phosphorus has been of evident interest to chemists and the determination of the structural parameters of such compounds was therefore begun almost immediately after the synthesis of phosphiran and its first homologues.

The microwave spectra of phosphiran, [^{13}C]phosphiran, *cis*- and *trans*-2-deuterophosphirans, and 1-deuterophosphiran were investigated, which made it possible to determine the bond lengths and angles in the phosphiran molecule, the result being presented in the Table. The dipole moment of phosphiran is 1.12 D.

The structure of crystalline 4-methyl-2,6,6-triphenyl-1-phospha-2,3-diazabicyclo[3.1.0]hex-3-ene (III, R=Ph), containing the phosphiran ring combined with the 1,2,3-diazaphospholan ring, was determined by X-ray diffraction[54]. It was found that the phosphorus atom has a distorted pyramidal configuration in this compound and that the plane of the three-membered ring makes an angle of 108.4° with the almost flat five-membered ring. The P–C bond lengths and the angle at the phosphorus atom in the phosphiran ring proved to be somewhat greater than the values in the Table.

Comparison with dimethylphosphine, which is an acyclic analogue of phosphiran and has $r(P-C) = 1.853$ Å, $r(P-H) = 1.445$ Å, $\alpha(CPC) = 99°12'$, and $\alpha(HPC) = 96°30'$,[55] shows that ring closure decreases the valence angles at the phosphorus atom and leads to a corresponding increase in the length of its endocyclic bonds. This effect is responsible for the increase of the *p* character in the bonds involving the phosphorus atom and of the *s* character of its unshared electron pair. Indeed, an independent estimate of the amount of *s* character of the hybrid atomic orbital of phosphorus in the P–H bond from the spin–spin coupling constant $^1J_{HP}$ yielded 5.3% for phosphiran, which is lower than the corresponding value for Me_2PH (6.5%).[17]

The bond lengths (*r*, Å) and angles (α, deg) in cyclopropane and its heteroanalogues XC_2H_4.[53]

Bond or angle	X					
	CH_2	NH	O	SiH_2	PH	S
r(C—C)	1.510	1.480	1.472	1.520	1.502	1.492
r(C—H)	1.088	1.082	1.082	1.081	1.093	1.078
r(C—X)	1.510	1.488	1.436	1.826	1.867	1.819
r(X—H)	1.088	1.000	—	1.480	1.428	—
α(CXC)	60.0	60.0	61.4	49.2	47.4	48.5
α(HCH)	115.1	116.7	116.6	120.0	114.4	116.0
α(C—CH_2)	150	159.4	159.5	143.9	149.5	151.7
α(HXC_2)	117.6	112.0	—	120.0	95.7	—
α(XCC)	60.0	60.2	59.2	65.4	66.3	65.8

In conformity with this, it has been noted[33] that the formation of a phosphiran ring with a phosphoryl group is accompanied by a decrease of the spin–spin coupling in the endocyclic P–C bonds and an upfield shift of the signal in the ^{31}P NMR spectrum. The stretching vibration frequency of the P=O bond increases under these conditions.

An interesting feature of the molecular structure of phosphiran is the fact that the *cis*-hydrogen atom of the methylene group is more remote from the phosphorus atom by 0.035 Å than the *trans*-hydrogen atom, while the angle between the CH bond and the plane of the ring is greater by 2.2° in the case of the *cis*-atom[17]. In order to elucidate the cause of this phenomenon, a microwave spectroscopic study was made of *cis*- and *trans*-2-methylphosphirans[56]. In this case too the substituent at the carbon atom in the *cis*-isomer is somewhat more remote from the phosphorus atom than in the *trans*-isomer, but the barriers to internal rotation in these isomers differ insignificantly, which is difficult to reconcile with the possible interaction through space between the proton at the phosphorus atom and the substituents at the carbon atoms of the phosphiran ring. The difference between the free energies of the isomeric 2-methylphosphirans, which is a measure of the stability of the isomeric forms, is also small ($\Delta F_{200K} = 0.13$ kcal mol^{-1}; *F* is lower for the *trans*-isomer). This also indicates the absence of an appreciable interaction through space. On the other hand, analysis of the change in the density matrix obtained by the extended Hückel method with adjustment for self-consistency with respect to charges[57] shows that all the atoms of the phosphiran molecule, including the methylene protons, are involved in the inversion of the phosphorus pyramid. This demonstrates the occurrence of an explicit interaction of the methylene protons with the proton at the phosphorus atom. Estimation of the barrier to inversion from the change in the orbital population yielded 39.9 kcal mol^{-1}, which is much larger than the analogous change for aziridine and agrees well with the usually observed high barriers in acyclic phosphorus compounds.

The calculation of the barriers to pyramidal inversion by the specially parametrised semiempirical CNDO/2 method without taking into account the *d* orbitals yielded a still higher value of phosphiran: 80.4 kcal mol^{-1}. The inclusion of the inverted centre in a small ring increases the barrier to inversion because of the corresponding increase in *s* character of the unshared electron pair of the heteroatom. In particular, it has been shown that the barrier increases in the series of phosphorus compounds investigated: trimethylphosphine < 1-methylphospholan < 1-methylphosphetan < phosphiran[58].

The phosphiran molecule provides an excellent possibility for the observation of the stretching vibrations of the C–P–C linkages in a small strained ring and the influence of this ring on the vibration frequency of the P–H bond. A study of the infrared spectra of phosphiran, 1-deuterophosphiran, and 2,2,3,3-tetradeuterophosphiran in the gas phase and of the Raman spectrum of phosphiran in the liquid phase has been reported[16]. The observed bands were identified on the basis of the frequency shifts in the deuterated derivatives, the data for the polarisation of the Raman lines, the contours of the infrared bands for the gas phase, and the characteristic group frequencies. Two bands were assigned to symmetrical vibrations of the P–C bonds in the ring: at 598.1 and 656.7 cm^{-1}. They have undergone a bathochromic shift relative to the analogous stretching vibrations in dimethylphosphine (664 and 710 cm^{-1}).

The 2291.4 cm^{-1} band in the spectrum of gaseous phosphiran was assigned to the stretching vibrations of the P–H bond; bearing in mind that the analogous band in the spectrum of dimethylphosphine is observed in the region of 2290 cm^{-1}, it was concluded[16] that the three-membered ring has an insignificant influence on the frequency of these vibrations. On the other hand, the deformation vibrations of the P–H bond in the gas phase (769 and 680.4 cm^{-1}) are observed at lower frequencies than those known for the analogous acyclic phosphorus compounds. For example, the corresponding band in the dimethylphosphine spectrum is in the region of 1146 cm^{-1}.[59]

In contrast to aziridine, where the frequency of the out-of-plane deformation vibrations of the N–H bond is higher than the frequency of the corresponding in-plane vibrations, in phosphiran the above relation is reversed from the analogous vibrations of the P–H bond[60]. This is undoubtedly caused by the smaller valence angles at the heteroatom in phosphiran (Table 1), as a result of which the steric hindrance to the displacement of the heteroatom proton from the symmetry plane is much smaller than the hindrance to the deformations within this plane.

The inversion barrier in phosphiran, estimated from the calculated force field of the molecule, is 33 kcal mol^{-1}.[60]

The thermodynamic functions of phosphiran have been calculated in terms of the rigid rotator–harmonic oscillator approximation[60]. They differ appreciably from the values obtained in another study[61] in terms of the analogous approximation but on the basis of an assignment of the infrared bands of phosphiran and related molecules differing somewhat from that described above[62].

A ^{31}P NMR study[14] showed that the phosphiran spectrum consists of a doublet with the centre at −341 p.p.m. relative to 80% phosphoric acid. The chemical shift of phosphorus thus proved to be the highest upfield shift among the values reported for phosphines. The spin–spin coupling constant $^1J_{PH} = 155$ Hz is unusually small. Each component of the doublet is split in a complex manner by interaction with the

methylene proton. A qualitative description of the proton NMR spectrum is also given.

The ^{31}P NMR spectra of substituted phosphirans yield additional evidence for their configurational stability. The existence of the *cis*- and *trans*-isomers of 2-ethylphosphiran has been demonstrated[15] by the presence in the spectrum of two doublets with different chemical shifts and slightly different spin–spin coupling constants $^1J_{PH}$. The more pronounced upfield character of the ^{31}P chemical shifts and their greater sensitivity to structural changes in substituted phosphirans compared with the analogous secondary and tertiary phosphines have also been noted.

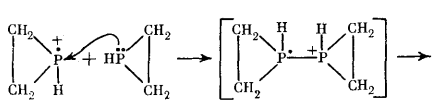
The chemical shifts in the ^{13}C NMR spectrum and the spin–spin coupling constants for 1-phenylphosphiran have been published[63]. The changes in these quantities with increase of the number of endocyclic C–C bonds and on ring opening are discussed in the same communication.

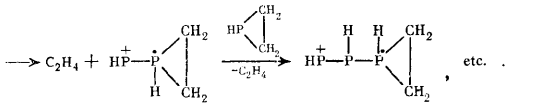
The results of mass-spectrometric studies of different types of phosphirans have been described: phosphirans with tricoordinate and tetracoordinate phosphorus, diphosphirans, element-substituted phosphirans, and others[15,29,64]. In all cases the spectra contain peaks due to molecular ions which are the most intense for monosubtituted phosphirans with tervalent phosphorus. The fragmentation of unsubstituted phosphiran and 1-deuterophosphiran is believed[15] to begin apparently with successive abstraction of the hydrogen atoms linked to the carbon atoms, while the P–H or P–D bonds remain unaffected. The introduction of methyl substituents into the molecule alters the preferred mode of fragmentation[15]. The mass spectra of all phosphirans with one phosphorus atom in the ring and of element-substituted phosphirans contain the peak of the fragment formed on rupture of both endocyclic phosphorus bonds. The fragmentation of 3,3-disubstituted 1,2-di-t-butyldiphosphirans takes place via the elimination of the t-butyl groups and their substitution by protons with subsequent formation of the $(M-C_4H_8)^+$ and $(M-2C_4H_8)^+$ ions[29].

The mass spectrum and the ion–molecule reactions of phosphiran and its mixtures with ammonia and deutero-, dideutero-, and trideutero-ammonia were also investigated by ionic cyclotron resonance spectrometry[64]. It was confirmed (see also Baudler and Saykowski[29]) that the most intense primary ions are the molecular ion M^+, the ions formed following the elimination of protons from the carbon atoms, $(M-2H)^+$ and $(M-3H)^+$, and also an ion with *m/e* 45 (PCH_2^+ or $HPCH^+$). There is no dominant secondary ion, as in the case of acyclic methylphosphines, and several ions in approximately equal proportions are formed. Another characteristic feature of phosphiran, found in the study of the influence of pressure (10^{-4}–10^{-6} mmHg) on the ionic ratios, proved to be a sharp decrease of the relative content of the molecular ions with increase of pressure (for methylphosphines, pressure has almost no influence on the content of the molecular ion).

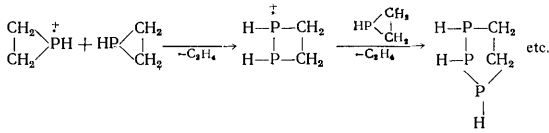
The ion–molecule reactions of phosphiran proceed mainly in three ways.

(a) The transfer of the P–H fragment from phosphiran to the molecular ion with evolution of ethylene and the formation of $R(PH)_n^+$ ions (where R = 1-phosphiranyl, $n = 1$–3), having an open phosphorus-containing chain or, which is more likely, having the structure of cyclic compounds with large rings formed as a result of the insertion of the P–H groups in the ring:

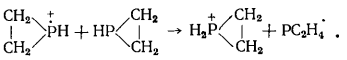




or

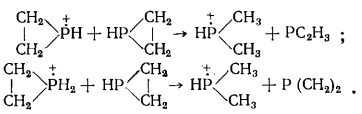


(b) The formation of protonated ions:

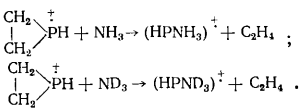


The determination of the rate constant for this reaction showed that phosphiran is protonated much more slowly than dimethylphosphine ($k = 0.54$ and 1.4×10^{-7} litre mole^{-1} s^{-1} respectively). The presence of the three-membered ring has a retarding influence on the rate of reaction (see Section IV).

(c) Ring decomposition:

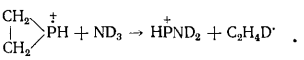


The reaction of ammonia and deuteroammonia with the molecular ion of phosphiran for an electron energy of 11 eV also entails the transfer of the P–H fragment and this process is not accompanied by deuterium exchange:



The reactions with NHD_2 and NH_2D take place analogously.

For an electron energy of approximately 15 eV and above, there is additiional abstraction of the proton or deuterium, for example:



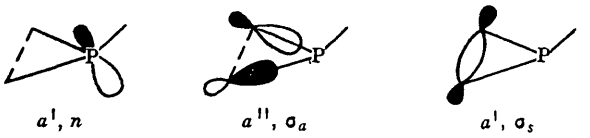
On the grounds that the molecular ion of phosphiran as well as the neutral molecule undergo PH transfer, it is concluded that the cyclic structure is retained in the molecular ion.

The interaction of phosphiran with the PH_3^+ radical-ion also proceeds as PH transfer with formation of the $P_2H_4^+$ radical-ion.

The relative stabilities of the cyclic onium ions $C_2H_4X^+$ have been investigated[65]. The study of the equilibrium $C_2H_4X^+ + HY \rightleftharpoons C_2H_4Y^+ + HX$ by the method of ionic cyclotron resonance made it possible to set up the series of increasing relative stabilities of ions for the following X: OH < Cl < Br < CH, $PH_2 < NH_2$.

The influence of angular strain in phosphiran on its electronic properties is of great interest to investigators. The study of the basicity and the ionisation potentials of phosphiran in relation to dimethylphosphine proved to be fruitful. The experimental photoelectron spectra of these compounds have been discussed[66] on the basis of *ab initio* quantum-chemical calculations. The removal of electrons from the highest occupied molecular orbitals with a′, a″, and a′ symmetries corresponds to the first three ionisation potentials of phosphiran and dimethylphosphiran. The orbital (*n*) with the highest energy is characterised by the dominant contribution of the unshared electron pair of the phosphorus atom

and the next two orbitals are characterised by the antisymmetric (σ_a) and symmetrical (σ_s) combinations of the *p* orbitals of the carbon atoms (Fig.1).



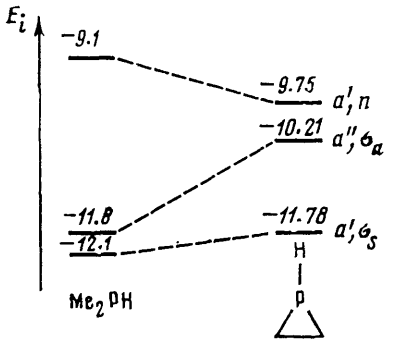


Figure 1. Correlation diagram for the orbital energies (in eV) of the three highest occupied molecular orbitals of dimethylphosphine and phosphiran[66].

The formation of the ring lowers the energy of the *n* molecular orbital by 15.4 kcal mol^{-1}. The stabilisation of this molecular orbital can be to a large extent accounted for by the enhanced *s* character of the unshared electron pair of the phosphorus atom in the three-membered ring. The repulsion of the electrons in the P–C σ-bonds increases with decrease of the C–P–C angle. The corresponding shift of electron density from P to C renders the phosphorus atom more positive, which also promotes the stabilisation of the *n* molecular orbital. The symmetrical combination of the π_{CH_2} orbitals of the two methylene groups is more strongly bonding than the symmetrical combination of the π_{CH_3} orbitals in dimethylphosphine. The hyperconjugation in phosphiran therefore destabilises the *n* molecular orbital to a lesser extent than in dimethylphosphine.

The lower-energy σ_a and σ_s orbitals are localised mainly at the carbon atoms. The shift of electron density from the P atom to C with decrease of the C–P–C angle, mentioned above, should destabilise both these orbitals. The mutual approach of carbon atoms enhances both the antibonding and the bonding interactions between them. As a result, the σ_a molecular orbital is most destabilised, while the energy level of the σ_s molecular orbital hardly changes.

The proton affinity of phosphiran is lower by 23.2 kcal mol^{-1} than that of dimethylphosphine[66]. The explanation is that, compared with the unstrained tetrahedral phosphorus atom in phosphonium salts, the angular strain in the protonated phosphiran is much greater than in its acyclic analogue. The enhanced *s* character of the unshared electron pair of the phosphorus atom in phosphiran and the shift of electron density in the P–C bonds from P to C also play an appreciable role.

Photoelectron spectroscopy combined with semiempirical quantum-chemical calculations has been used to investigate the electronic structures of three-membered heterocycles containing more than one phosphorus atom[67].

Investigators were naturally interested in the structural characteristics and physical properties of phosphiran relative to other known three-membered heterocycles which are derivatives of elements in Period II and III in Mendeleev's Table. This Table shows a steady decrease of the C–C bond length with increase of the atomic number of the element within the limits of each Period. This effect has been explained[68] by regarding the XC_2H_4 heterocycle as a donor–acceptor complex of ethylene C_2H_4 in the ground state and the fragment X in the valence state with the $(np_x)^2$ $(np_z)^0$ configuration of the endocyclic heteroatom ($n = 2$ or 3) (Fig.2).

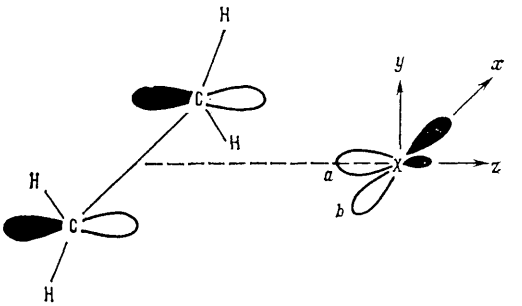


Figure 2. The heterocycle XC_2H_4 in the form of the $C_2H_4 + X$ donor–acceptor complex.

The C–C bond is weakened as a result of the transfer of electron density from the occupied *b* orbital of the fragment X (*yz* symmetry plane) to the vacant π* orbital of C_2H_4 and from the occupied π orbital of C_2H_4 to the vacant *a* orbital of X. The degree of such transfer is determined mainly by the energy levels of the *a* and *b* orbitals of X. Calculation of these levels by the *ab initio* SCF-MO method yielded a satisfactory explanation even for the non-uniformity of the shortening of the C–C bond within each Period.

Calculation of certain structural parameters of three-membered heterocycles, including phosphiran and the phosphiranium ion by the MNDO method without taking into account the *d* orbitals was used by Dewar and Ford[69] to set up the "π-complex character" series for these rings. The above authors expressed the view that, depending on the electronegativity and other properties of X, the compounds XC_2H_4 can constitute a continuous series, at one end of which there are the "classical" three-membered rings of the type of cyclopropane, while at the other there are π-complexes of the olefin–transition metal type. In the latter the intramolecular transfer of electron density from C_2H_4 to X greatly exceeds the reverse transfer. On the basis of the calculation of several criteria for the estimation of the "π-complex character" of the compounds XC_2H_4, series based on decreasing "π-complex character" of the heterocycles were established. Since compounds with X = PH and SiH_2 were found to be at the very end of this series, even beyond CH_2, phosphiran and siliran must be classified as the most typical "classical" three-membered rings in which electron transfer from X to C_2H_4 is the dominant feature.

It has been shown[53] that the C–C bond length in a three-membered heterocycle is determined mainly by the transfer of electron density from the *b* orbital of X to the π* orbital of ethylene. Increase of the electronegativity of X diminishes the effect of such transfer. As a result, the C–C bond is shortened and the angle β between the axis of this

bond and the normal to any of the CH_2 planes increases. The corresponding quantum-chemical calculations have shown that the overlap population of the C–C bond then increases and that of the X–C bond diminishes.

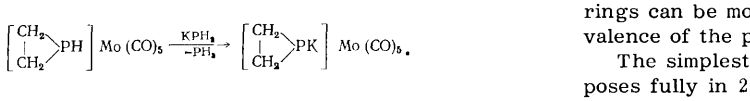
Several studies have been devoted to calculations on hypothetical molecules, which have not as yet been obtained, incorporating a three-membered phosphorus-containing ring, in particular cyclic spiro-compounds with a bridgehead phosphorus atom. A qualitative examination of the interaction of the *p* orbitals of the carbon atoms with the *d* orbitals of the phosphorus atom in symmetrical compounds with two mutually perpendicular rings[70] permits the conclusion that some of these systems are stable. Analogous systems have been considered quantitatively in a study[71] where the geometries and heats of formation of the individual spiro-compounds were calculated by the MINDO/3 method with minimisation of the total energy. The relative instability of these compounds is explained by the high energy level of the highest occupied molecular orbital and hence by their high reactivity towards electrophiles. Stabilisation can be achieved by the addition of electron-accepting groups to the central atom. The inclusion of the 3*d* orbitals of the phosphorus atom in the calculation greatly reduces the level of the highest occupied molecular orbital, thereby increasing the stability of the entire bicyclic system.

Thus the study of the structural characteristics and physical properties of compounds containing the phosphiran ring is being continued using all modern experimental and computational methods.

IV. CHEMICAL PROPERTIES

1. The Acidity of Phosphiran and Its Derivatives

Since direct measurements of the acidity of P-unsubstituted phosphirans have not been made, the conclusion that the mobility of the hydrogen atom linked to phosphorus is low can be reached only at a qualitative level on the basis of attempts to carry out exchange reactions. When phosphiran is treated with potassium in liquid ammonia or with ethyl-lithium in ether, hydrogen is not evolved. Nor does the exchange reaction occur with potassium phosphide in dimethyl ether. Such exchange does take place, however, in a complex of phosphiran with molybdenum carbonyl, i.e. pentacarbonylphosphiranmolybdenum(0), approximately 80% of the calculated amount of phosphine being evolved[72]:



^{1}H NMR data have shown that in methanol there is no rapid exchange of the hydrogen atom attached to phosphorus for the methanol protons[14]. Thus in this respect phosphiran does not differ from acyclic secondary phosphines[73].

2. The Basicity of Phosphiran and Its Derivatives

The few available literature data show that the phosphorus atom in the three-membered ring is much less basic than in acyclic phosphine and than the nitrogen atom in a similar ring. For example, the calculated potential energies of atomic interactions[57] have shown that the density of the free electron pair of the phosphorus atom in phosphiran is delocalised over the carbon atoms of the ring to a much greater extent than the electron density of nitrogen in aziridine. Only 62.3% of the free electron pair density is localised at the phosphorus atom, in contrast to the 76.3% at the nitrogen atom of aziridine.

This type of delocalisation is even more pronounced in 1-methylphosphiran, where only 57.1% of the free electron pair density remains at the phosphorus atom and Petersen and Brisotti[57] suggested that this compound should be the weakest base among the compounds which they examined (apart from those indicated, they also investigated 1-methyl- and 1-chloro-aziridines), provided that the basicity is correlated with the localisation of electron density at the heteroatom.

Comparison of the properties of the heteroatom in phosphiran and other three-membered rings containing elements in the Second and Third Periods (C, N, O, S, and Si) on the basis of quantum-chemical calculations by the CNDO method[53] showed that, with increase of the atomic number of the element, there is a systematic increase of the negative charge on the heteroatom in each Period and its decrease in each Group of the Periodic System. Thus the charge on the phosphorus atom of phosphiran is much less negative than on the nitrogen atom of aziridine (+0.109 and −0.167 respectively) and on the sulphur atom in thi-iran (−0.103), but is less positive than on the silicon atom in siliran (+0.316).

The decrease of the basicity of the heteroatom on passing from acyclic compounds to three-membered heterocycles is a general property, as shown by studies of the basicity of rings with N, O, S, and P heteroatoms and also of dimethyl-substituted acyclic compounds of these elements (Me_2NH, Me_2O, Me_2S, and Me_2PH) by ion cyclotron resonance[66]. The decrease of proton affinity is explained by the increase of the amount of s character of the orbtials of the free electron pair of the heteroatom and by the redistribution of electron density in the C–X bond as well as the increase of the angular strain on protonation, since this should entail a transition from a pyramidal to a tetrahedral angle. The influence of angular strain is the dominant factor in phosphiran, which has the smallest C–X–C angle. On passing from dimethylphosphine to phosphiran, a particularly sharp decrease of basicity is observed (the difference between proton affinities is in this instance 23.2 kcal mol^{-1}, while for the N, O, and S analogues it is only 3–5 kcal mol^{-1}).

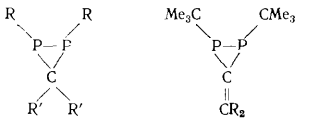
3. The Opening of the Three-membered Ring

(a) *Thermolysis of the phosphiran ring.* The high ring strain, which is a characteristic property of rings with three and four members, is also manifested in phosphirans, whose rings can be more or less readily opened depending on the valence of the phosphorus and the nature of the substituents.

The simplest phosphiran is thermally unstable and decomposes fully in 24 h even at room temperature on storage without a solvent, giving rise to ethylphosphine (15%), ethylene (6%), and an involatile viscous liquid. The decomposition in methanol at room temperature is slow[14].

The diphosphirans with tervalent phosphorus known at the present time showed a tendency towards dimerisation with formation of 1,2,4,5-tetraphosphacyclohexanes. The thermal stability of diphosphirans of this type depends on the bulk of the substituents and increases appreciably even on substitution of the hydrogen atoms at a ring carbon atom by methyl groups. Thus the conclusion that the heterocycle (XII, R = Ph, R′ = H) is formed also on interaction of 1,2-diphenyl-1,2-bis(trimethylsilyl)diphosphine with di-iodomethane at −30 °C was based solely on the appearance of a weak signal in the ^{31}P NMR spectrum of the reaction mixture with a chemical shift characteristic of the phosphorus atom in a three-membered ring, whereas compound (XII, R = Ph,

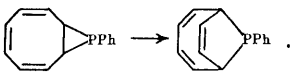
R′ = Me) can be obtained at −30 °C in a yield of approximately 10% and is stable in benzene at this temperature for several days[28]. The still more stable diphosphirans (XII, R = t-Bu) can be vacuum-distilled at approximately 30 °C without decomposition. However, whereas the diphosphiran (XIIa) dimerises at room temperature in a pure form in several hours (more slowly in solution and at −78 °C the dimerisation ceases [29,30]), compound (XII, R = t-Bu, R′ = Me) can be maintained at room temperature in an inert gas atmosphere for months and can be briefly heated to as much as 200 °C without visible decomposition; in air the last two compounds both rapidly oxidise without igniting[29]. On the other hand, the diphosphiran (XII, R = iso-Pr, R′ = H) cannot be obtained at all—the six-membered dimer is formed immediately[30]:



(XII) (XIII)

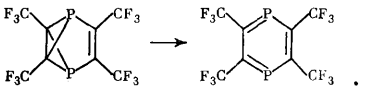
An analogous behaviour has been observed also for diphosphirans (XIII) with an exocyclic C = C bond. The methylenediphosphiran (XIII, R = H) begins to decompose in the reaction mixture already at −50 °C, so that it was possible to obtain it only with a purity of 70%, whereas its analogues with methyl or *p*-chlorophenyl groups are comparatively stable and have been isolated in a pure form by high-vacuum distillation or fractional cyrstallisation[11].

The bicyclic phosphiran with condensed rings 9-phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene can be stored in an inert atmosphere with cooling over a period of one year almost without changes, but, on raising the temperature the three-membered ring expands with formation of 9-phenyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene (XXXVIII), which has been isolated in a high yield[19,20]:



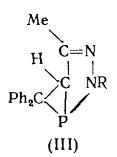
(I) (XXXVIII)

When the phosphorus analogue of benzvalene, which is stable at room temperature, is heated or illuminated with light from a low-pressure mercury lamp (λ = 2537 Å), it is reconverted into a 1,4-diphosphabenzene derivative (X) by a sigmatropic rearrangement (in hexafluorobenzene at −198 °C the half-life of the reaction is approximately 75 min[25,27]):



(XI) (X)

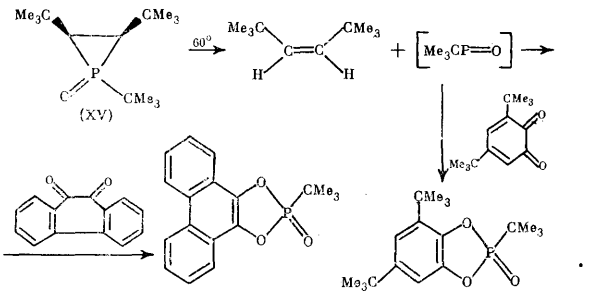
Despite the presence of tervalent phosphorus in the three-membered ring, derivatives of 1-phospha-2,3-diazabicyclo-[3.1.0]hex-3-ene exhibit an appreciable thermal stability, melting without decomposition at 135° and 145 °C [for R = Ph and MeCO respectively][21].



(III)
R=Ph, MeCO

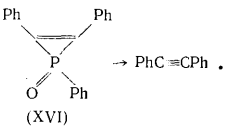
In the search for a quantitative approach to the problem of the comparative stabilities of the three-membered rings XC_2H_4 (X = CH_2, O, NH, PH, PH_3, or S), a group of Romanian investigators[31] calculated the enthalpies of decyclisation of the above compounds in several ways by an additive scheme using the tabulated bond energies and found that the ring with X = PH_3 has the highest positive enthalpy of decyclisation, i.e. derivatives of phosphiran with a pentavalent phosphorus atom, which had not yet been obtained at the time of the publication of the above study, should be resistant to thermal ring opening. Experimental data have shown that the stability of the ring depends on the structural features of each specific compound.

For example, *cis*-1,2,3-tri-t-butylphosphiran oxide (XV) is stable at room temperature but decomposes on heating in perdeuterobenzene at 60 °C, giving a quantitative yield of *cis*-2,2,5,5,-tetramethylhex-3-ene, i.e. the thermolysis is stereospecific. The second decomposition product, the unstable t-butylphosphinidene oxide with a dicoordinate phosphorus atom, cannot be detected when the thermolysis of the oxide (XV) is carried out in the presence of 1,2-bis-(trimethylsilyl)acetylene, 2,3-dimethylbutadiene, diacetyl, benzil, or *N*-(2,2-dimethylpropylidene)-t-butylamine, but 2-t-butylphenanthro[9,10-*d*]-1,3,2-dioxaphosphole oxide was obtained in 50% yield in the presence of 9,10-phenanthrenequinone, while 2,4,6-tri-t-butylbenzo-1,3,2-dioxaphosphole oxide is formed in a quantitative yield in the presence of 3,5-di-t-butyl-*o*-benzoquinone, which confirms the formation of a species with a dicoordinate phosphorus atom[32]:



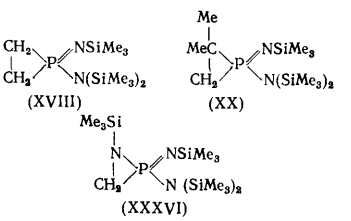
(XV)

1-Oxo-1,2,3-triphenylphosphiren (XVI) is cleaved analogously at 120 °C *in vacuo* (10^{-5}–10^{-6} mmHg), forming diphenylacetylene[35]:



(XVI)

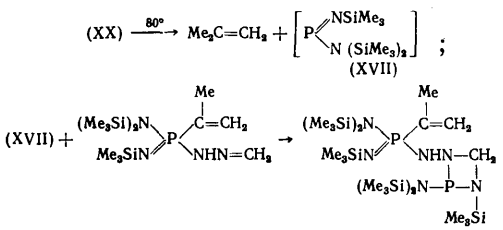
The positive influence of the steric shielding of the molecule on the thermal stability of the ring can be clearly traced in phosphirans with an exocyclic phosphazo-group and bulky substituents. Thus 1-[bis(trimethylsilyl)amino]-1-trimethylsilyliminophosphiran (XVIII), unsubstituted in the 2- and 3-positions, decomposes fairly rapidly at room temperature[38], while its analogue (XX) with two methyl groups in the 2-position[40] and the azaphosphiridine (XXXVI) with a bulky trimethylsilyl group at the ring nitrogen atom[38] are stable at room temperature:



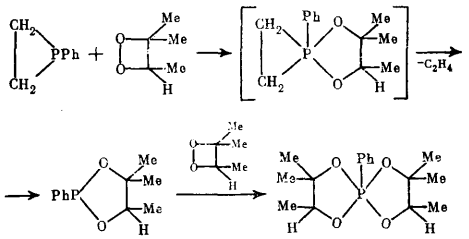
(XVIII) (XX)

(XXXVI)

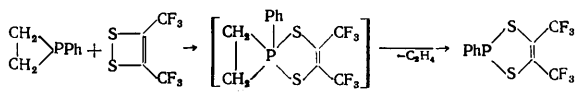
On heating to 80 °C, the phosphiran (XX) decomposes to 2-methylprop-1-ene, which has been characterised by infrared spectroscopic data, and the aminoiminophosphine (XVII), which undergoes further reactions as a result of the addition to the second product formed on synthesis of compound (XX):



In cyclic spirophosphoranes with a pentacoordinate phosphorus atom a three-membered phosphorus-containing ring has a low thermal stability. For example, in the reaction of 1-phenylphosphiran with 2,3,3-trimethyldioxetan, a cyclic spirophosphorane can be detected at −80 °C by ^{31}P NMR. At the above temperature the spectrum of the reaction mixture remains unchanged in the course of two weeks, but, on raising the temperature, ethylene is evolved and the signal assigned to the resonance of the phosphorus nucleus of the phosphorane with the three-membered phosphorus-containing ring disappears[43]:



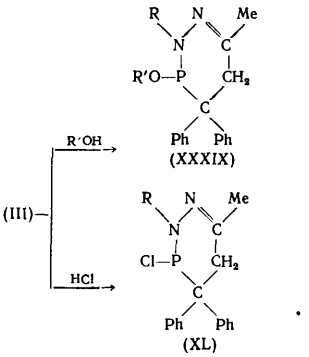
When 1-phenylphosphiran was treated with 3,4-bis(trifluoromethyl)dithieten at −78 °C, only ethylene and 2-phenyl-4,5-bis(trifluoromethyl)-1,3,2,-dithiaphospholen were obtained, i.e. the intermediate cyclic spirophosphorane decomposes even at this low temperature[18,74]:



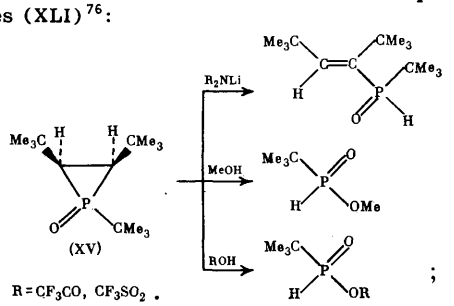
The decomposition proceeds via a concerted and not a two-stage mechanism, since the reaction involving *cis*-2,3-dideutero-1-phenylphosphiran yields, 1,2-dideuteroethylene containing mainly the *cis*-isomer (95 : 5).[18]

(b) *Ring opening on treatment with chemical reagents.* The phosphiran ring of the unsubstituted compound is rapidly decomposed by acidic and basic agents. Even at reduced temperatures, phosphiran is rapidly decomposed by hydrogen chloride, giving rise to 90% of ethylene, 20% of phosphine, 5% of ethylphosphine, and a yellow solid which is mainly a polymeric phosphine[14]. On interaction with sulphur dioxide at 0 °C, ethylene and a polymeric product are also formed[75]. The interaction of phosphiran with potassium in liquid ammonia gives rise, as a result of ring cleavage, to a mixture of the anions of a series of phosphines. Rupture of the phosphiran ring also occurs on treatment with methyl-lithium in ether[72].

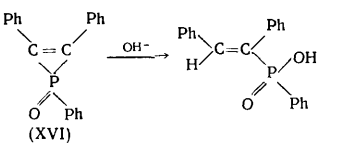
On heating with alcohols or on treatment with hydrogen chloride, the three-membered ring is also cleaved in derivatives of 1-phospha-2,3-diazabicyclo[3.1.0]hex-3-ene and the monocylic compounds (XXXIX) and (XL) are formed[22]. Under these conditions the P–C bond ruptured is that whose approach by the reagent apparently involves the smallest steric hindrance:



On the other hand, *cis*-1,2,3-tri-t-butylphosphiran oxide is very stable at room temperature in concentrated hydrochloric acid, trifluoroacetic acid, and trifluoromethanesulphonic acid and also in concentrated aqueous alkali, being decomposed only slowly by lithium diethylamide or piperidide with formation of t-butyl(1,2,-di-t-butylvinyl)phosphine oxide[34]. In boiling methanol the oxide (XV) is converted in 20 h into the monomethyl ester of t-butylphosphonous acid[33], while its thermolysis in trifluoroacetic or trifluoromethanesulphonic acid results in conversion into the corresponding anhydrides (XLI)[76]:



Hydrolysis of 1,2,3-triphenylphosphiren oxide by an aqueous solution of sodium hydroxide to phenyl(1,2-diphenylvinyl)phosphinic acid confirms the structure of this phosphiren derivative[35]:



2-Cyano-1,1-diethylphosphiranium chloride is converted on hydrolysis into a mixture of 2-cyanoethyl(diethyl)phosphine and diethylphosphinic acid, which is difficult to separate[41].

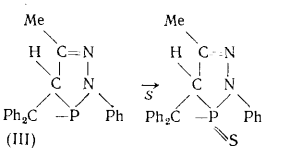
4. Reactions Occurring with Retention of the Phosphiran Ring

When phosphiran reacts with the *N*-methylpyridinium salt of pentacarbonylmolybdenum iodide, a molybdenum complex is formed in which phosphiran is one of the ligands, namely pentacarbonylphosphiranmolybdenum(0):

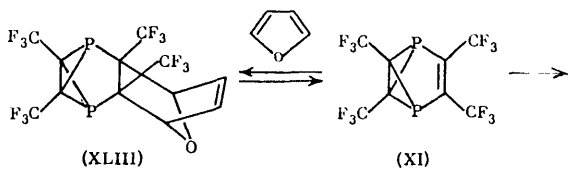


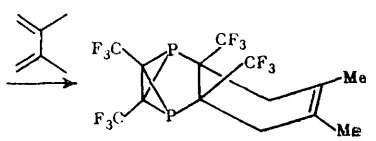
Phosphiran can displace also other ligands from molybdenum complexes: for example, pentacarbonylnorbornadienemolybdenum(0) and tricarbonylcyclohexatrienemolybdenum(0) give rise respectively to tetracarbonylbis(phosphiran)molybdenum(0) and tricarbonyltris(phosphiran)molybdenum(0). The complexes have been characterised by ^{1}H and ^{31}P NMR data[72]

The addition of sulphur to a derivative of 1-phospha-2,3-diazabicyclo[3.1.0]hex-3-ene also takes place with retention of the three-membered ring and has given rise to the first representative of a phosphiran with a P–S bond[22]:



The phosphorus analogue of benzvalene (XI) is capable of entering into the Diels–Alder reaction as the dienophile, forming, for example, with 2,3-dimethylbutadiene, the adduct (XLII), to which the *exo*-configuration has been attributed by analogy with the adduct obtained from benzvalene. Reaction with furan results in the formation of an equilibrium mixture of the initial compound (XI) and the adduct (XLIII):

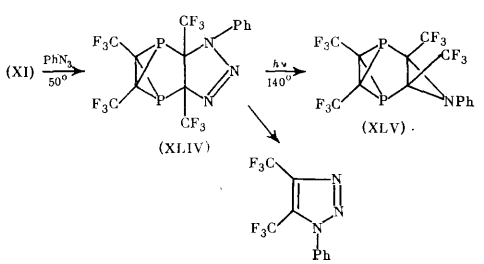




(XLII)

When the adduct is dissolved in n-pentane, a solution is obtained whose ^{19}F NMR spectrum reveals the presence of compound (XI), equilibrium being established extremely rapidly at 70 °C.

Phenyl azide also adds to the double bond of the tricyclic compound (XI), giving the adduct (XLIV) with an additional triazoline ring, which evolves nitrogen on photolysis or heating at 140 °C and is converted into diphosphabenzvalenoaziridine (XLV); it has been shown by ^{19}F NMR that the initial compound (XI) is then obtained together with compound (XLV). Chromatography on silica gel entails the decomposition of this adduct (XLIV) with formation of 1-phenyl-4,5-bis(trifluoromethyl)triazole[27]:



---oOo---

The chemistry of heterocyclic phosphorus compounds is now passing through a period of vigorous development. The present review has dealt with the results of studies on three-membered organophosphorus heterocycles. It is of interest to examine the synthesis and properties of four-membered phosphorus-containing heterocycles.

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Phenyl-substituted Polyheteroarylenes

V.V.Korshak and A.L.Rusanov

The fundamental methods of synthesis of polyheteroarylenes containing phenyl substituents in the heterocycles, formed in the course of the polycyclocondensation process, are examined. The influence of the phenyl substituents on the principal characteristics of the polyheteroarylenes is analysed. The likely usefulness of the introduction of phenyl substituents into polyheteroarylenes, in the sense of increasing their solubility, thermoplasticity, and resistance to thermal oxidation, is demonstrated.
The bibliography includes 112 references.

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I. INTRODUCTION

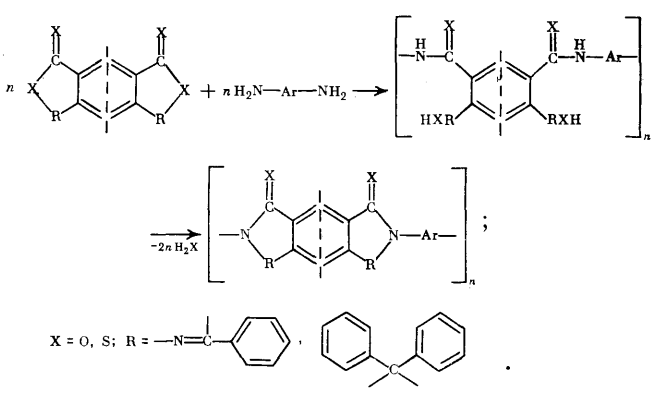
The development of a number of fields of modern technology has led to the necessity of synthesising thermostable polymeric materials and hence new thermostable polymers. Numerous studies designed to synthesise thermostable macromolecular compounds, both in the USSR and abroad, have resulted in the development of a series of organoelemental[1,2] and aromatic carbochain polymers[1,3-8], but aromatic polymers containing various heterocycles in the main macromolecular chains, namely polyheteroarylenes, have come to be most widely used[1,3,4,6,7,9,10-12].

One of the achievements in the chemistry of polyheteroarylenes has been the development of multistage methods of their synthesis in which the first stages are carried out under mild conditions, the resulting prepolymers are isolated and used to make the required articles, after which thermal cyclisation is carried out directly in the finished article[1,4,9]. This approach has been used widely and successfully in the synthesis of polyimides[13,14], polyazoles, and polybenzazoles[15-18] and also a series of other polyheteroarylenes. Together with unquestionable advantages, the multistage method of synthesis of polyheteroarylene suffers from a series of significant disadvantages, among which the main one is the instability of the prepolymers[13,14] and also the lack of technological procedures for the thermal cyclisation processes and the impossibility of secondary processing of the polyheteroarylenes. As a result, in the middle 1960s a tendency arose in the chemistry of polyheteroarylenes to impart to these systems solubility in organic solvents in the final stage. Solubility in inorganic solvents and hence improved capacity for being converted into articles can be imparted to polyheteroarylenes in various ways—by introducing "hinged" groups into the main chain of the macromolecules, by synthesising macromolecules with the most asymmetric structure possible[3,19], and by synthesising polymers with bulky side groups—the "card" polymers[20-22]. However, the approach involving the introduction of phenyl side groups into the polyheteroarylenes, i.e. the synthesis of phenyl-substituted polyheteroarylenes, has come to be most widely employed. Phenyl substituents can be introduced by using monomers containing phenyl groups either in fragments which do not change in the course of the polycyclisation reaction[23,24] or in functional groups or fragments involved in the formation of the heterocycle. Phenyl substituted polyheteroarylenes obtained by the second of the above two procedures will be examined in this review.

II. PHENYLATED ANALOGUES OF POLYIMIDES

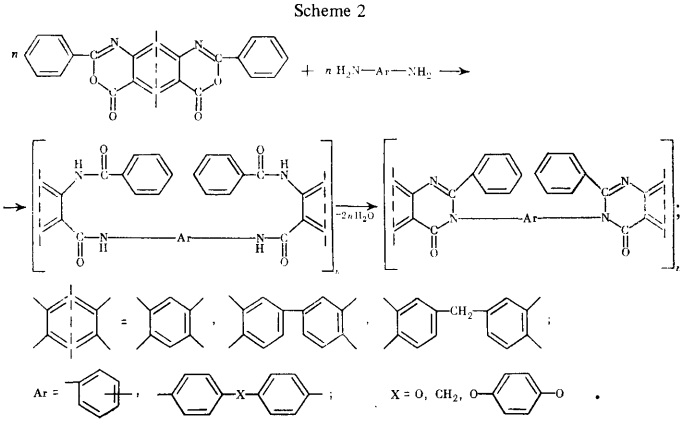
A large group of reactions involving the synthesis of phenyl-substituted polyheteroarylenes, obtained from monomers containing phenyl substituents in functional groups, can be represented by a general scheme similar to that for the synthesis of polyimides[13,14], i.e. involving the interaction of cyclic electrophilic monomers with diamines accompanied by ring opening and subsequent cyclodehydration of the resulting *o*-substituted polyamides (Scheme 1).

Scheme 1



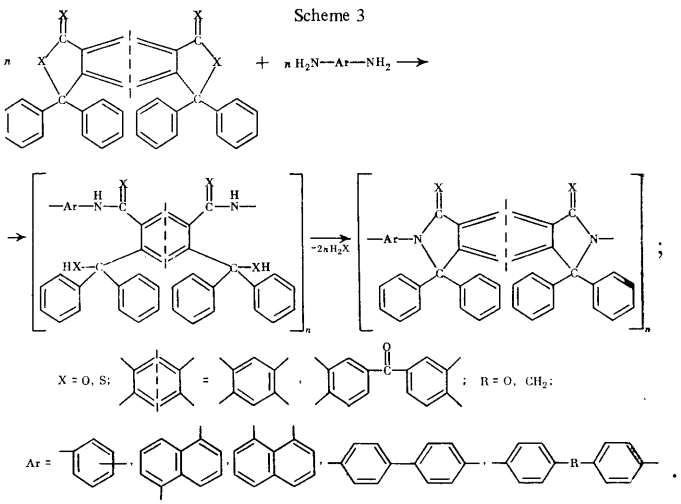
The first polyheteroarylenes obtained in accordance with Scheme 1 were phenyl-substituted polyquinazolinones, whose synthesis was achieved by the interaction of bis(2-phenylbenzoxazin-4-ones) with aromatic diamines[25–29] in accordance with Scheme 2.

Scheme 2



The reduced electrophilic reactivity of bis(2-phenylbenzoxazinones) compared with the dianhydrides of tetracarboxylic acids[30] necessitates the synthesis of phenyl-substituted polyquinazolinones under the conditions of high-temperature polycyclocondensation in polyphosphoric acid (PPA) or phenolic solvents[25–29]. The fact that the polycyclocondensation processes are carried out at 200° ± 20 °C combined with the ease of formation of six-membered heterocyclic systems makes it virtually impossible to isolate the intermediate poly(*o*-benzamido)amides and results in the occurrence of cyclisation reactions under the conditions of polymer chain propagation reactions. It is most useful to employ di(4-aminophenyl) ether and di(4-aminophenyl)methane as aromatic diamines. These substances are the most basic in the series of aromatic diamines[31]. Furthermore, the presence of "hinged" groups in these compounds determines the enhanced flexibility of the macromolecules obtained on their basis. Phenyl-substituted polyquinazolinones synthesised from these diamines are soluble in acid and phenolic solvents and are highly viscous, which makes it possible to prepare strong elastic films on their basis. Phenyl-substituted polyquinazolinones exhibit a comparatively high thermal stability—according to the results of dynamic thermogravimetric analysis (DTGA), the polymers do not undergo degradation in air up to 420 °C.

Scheme 3



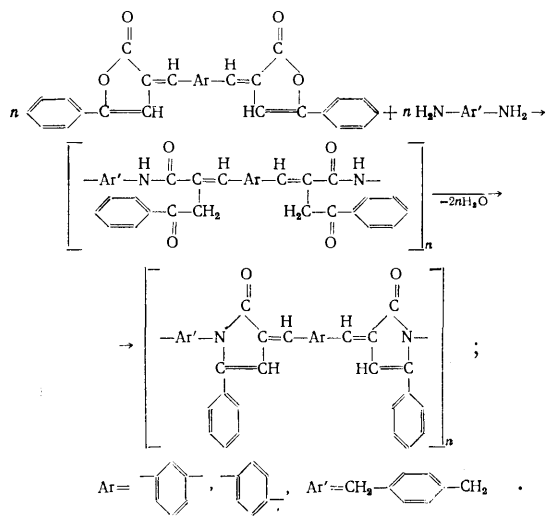
Phenylated polyimidines have been obtained by the reaction of phenylated phthalides[32–35] or their thio-analogues[33] with aromatic diamines in accordance with Scheme 3.

Like benzoxazinones, phthalides are comparatively weakly electrophilic[36,37] and react with amines, particularly aromatic amines, extremely slowly even in the presence of two phenyl substituents in the 3-position of the phthalide ring. For this reason, phenylated polyimidines are synthesised in accordance with Scheme 3 at high temperatures (180–350 °C), which precludes in its turn the isolation of the intermediate *o*-substituted polyamides and polythioamides. Regardless of whether the polyimidines were synthesised in the melt or in solvents, for example in PPA, nitrobenzene, biphenyl, dixylylethane, trichlorobenzene, or *m*-cresol, the polymers obtained have comparatively low viscosity characteristics (the maximum value of η_{log} of their solutions did not exceed 0.3 dl g^{-1}). At the same time the polyimidines were readily soluble in organic solvents—$CHCl_3$, dimethylformamide (DMF), and CCl_4—and exhibited a high thermal stability, losing 10% of the initial mass at 400–525 °C in air and at 450–560 °C in an inert medium[32–35]. These advantages of polyimidines are responsible for the interest in the synthesis of high-molecular-weight systems of this type. One of the possible ways of solving the problem of such synthesis consists in the employment as monomers of thio-analogues of phthalide compounds more reactive than the oxo-compounds[33].

Products similar in structure and properties to the polymers obtained in accordance with Scheme 3 were synthesised by the homocondensation of 6-amino-3,3-diphenylphthalide[38] and 3-(*p*-aminophenyl)-3-phenylphthalide[39] in PPA, nitrobenzene, trichlorobenzene, or dixylylethane.

The synthesis of phenylated polypyrrolinones by the reaction of 2,2-diphenyl-substituted bis(but-3-en-4-olides) with diamines[40] (Scheme 4) is fairly closely related to the reactions described in a general form by Scheme 1.

Scheme 4

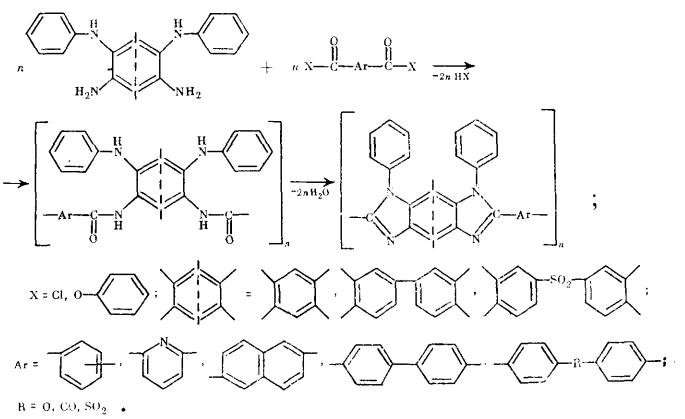


The first stage of the process at a low temperature in *m*-cresol led to the formation of polyamides with keto-side groups. When the process was carried out at 80 °C in the presence of acid catalysts (H_3BO_3, HCl, or CH_3COOH) or at 160 °C in the absence of catalysts, phenyl-substituted polypyrrolinones were obtained. Both polyamides with keto-substituents and phenylated polypyrrolinones are soluble in polar solvents (*m*-cresol, nitrobenzene, and DMF), but their viscosity characteristics are low (the maximum η_{log} of their solutions do not exceed 0.5 dl g^{-1}) and they have a low thermal stability, which makes these systems less interesting.

III. PHENYLATED POLYBENZAZOLES, POLYTRIAZINES, AND POLYQUINOXALINES

Together with the synthesis of phenyl-substituted polyheteroarylenes by reactions analogous to those used in the synthesis of polyimides, the synthesis of phenyl-substituted polybenzazoles in accordance with the general scheme for the synthesis of these systems[16-18], has attracted the attention of investigators. In the series of phenyl-substituted polybenzazoles, the synthesis of poly(*N*-phenyl)benzimidazoles in accordance with Scheme 5 has attracted most attention[28,41-53].

Scheme 5

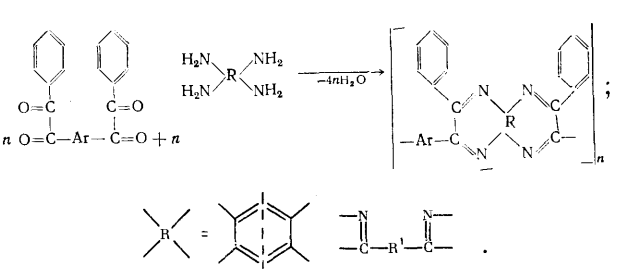


The first studies designed to obtain poly(*N*-phenyl)-benzimidazoles were associated with the reaction of bis(*N*-phenol-*o*-phenylenediamines) with the diphenyl esters of dicarboxylic acid; the process was carried out initially in the melt and was followed by the subsequent high-temperature additional cyclisation of the solid mass *in vacuo* (the Marvel reaction" [41-44]). The poly(*N*-phenyl)benzimidazoles obtained were distinguished by relatively low viscosity characteristics (the η_{int} of 0.5% solutions in HCOOH at 25 °C were in the range 0.64–0.86 dl g^{-1}),[44] which precluded the formation from them of articles with effective deformation-strength characteristics.

In order to increase the viscosity characteristics and hence the molecular weights of these polymers, attempts were made to synthesise poly(*N*-phenyl)benzimidazoles by a two-stage process. The first stage involved the interaction of bis(*N*-phenyl-*o*-phenylenediamines) with the dichlorides of dicarboxylic acids under the conditions of low-temperature polycondensation in dipolar aprotic solvents[28,42-52]. The second stage involved the cyclisation of poly(*o*-phenylamino)-amides under the conditions of thermal solid-phase polycyclisation[42-52]. When the synthesis of poly(*o*-aminophenyl)amides is carried out in amide solvents[28,45-49], high-molecular-weight systems, forming strong elastic films, are obtained; polymers with still higher molecular weights are formed when the polycondensation is carried out in sulpholan[51,52], which does not enter into side reactions with aromatic dicarboxylic acid dichlorides. The poly(*o*-aminophenyl)amides are usually cyclised to poly(*N*-phenyl)benzimidazoles by the solid-phase heat treatment of these systems[45-52]; this results in the formation of high-molecular-weight film-forming products which are soluble in acid and phenolic solvents. The cyclisation can also be achieved in PPA [45-47] or, more effectively, by adding hydrogen chloride or other acid catalysts to the reaction solutions of poly(*o*-aminophenyl)amides and then heating the latter at 160–170 °C.[28,45-47] Unfortunately the catalytic polycyclisation of poly(*o*-aminophenyl)amides has not come to be widely used, although there is no doubt about the likely usefulness of the method.

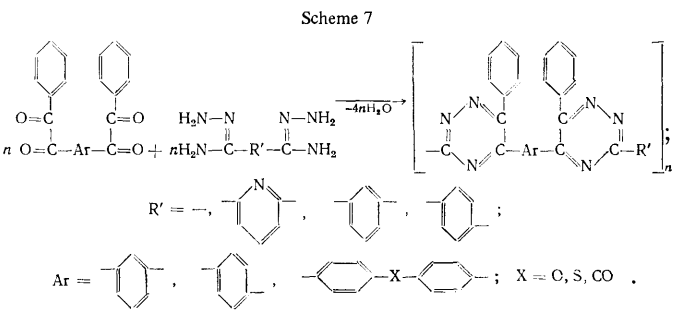
Detailed comparison of the properties of poly(*N*-phenyl)-benzimidazoles and unsubstituted polybenzimidazoles[42,53] showed that the introduction of phenyl substituents improves the solubility of the polymers and their resistance to thermo-oxidative degradation with the simultaneous decrease of their softening temperatures and thermal stability in an inert medium. The latter factor is due to the ease of abstraction of the phenyl substituents from the nitrogen atoms of the benzimidazole ring as a consequence of the lack of conjugation between the heterocycle and the substituent[53,54]. In the light of these data, the synthesis of polyheteroarylenes containing phenyl substituents at a carbon atom is preferable. A large family of such polymers has been obtained as a result of the reaction of tetrafunctional nucleophilic compounds (bis-*o*-phenylenediamines[55] and dicarboxylic acid bis-amidrazones[55,56]) with bisphenylglyoxalyl derivatives[55,57] in accordance with the general Scheme 6.

Scheme 6



The interaction of dicarboxylic acids bisamidrazones with bisphenylglyoxalyl derivatives in accordance with reaction (7) results in the formation of poly-*asym*-triazines[57-70].

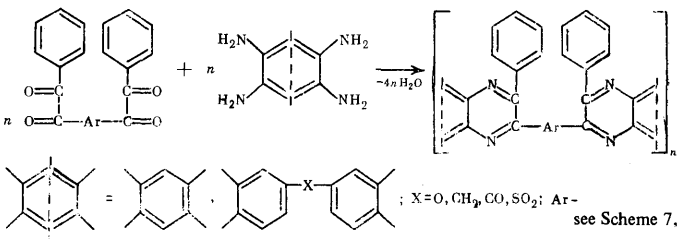
Scheme 7



The synthesis of poly-*asym*-triazines takes place smoothly in *m*-cresol and a number of other solvents even at room temperature. Fully aromatic phenylated poly-*asym*-triazines are characterised, depending on their structure, by a high or limited solubility in acid and phenolic solvents and also in chloroform, dimethyl sulphoxide (DMSO), dimethylacetamide (DMA), and other dipolar aprotic solvents. These polymers have high viscosities and hence high molecular weights which determine the possibility of preparing from them films, adhesives, and binders for glass plastics[63,66] capable of being used for a long time at 260 °C. Poly-*asym*-triazines soften at 270–330 °C and, in contast to unsubstituted poly-1,2,4-triazines, are characterised by a comparatively high resistance to isothermal thermal ageing in air, because the most thermostable representatives of this class of polyheteroarylenes lose 20–25% of the initial mass in 45 h at 290 °C. Polyphenylquinoxalines, which are the products of the interaction of bis(*o*-phenylenediamines) with bisphenylglyoxalyl

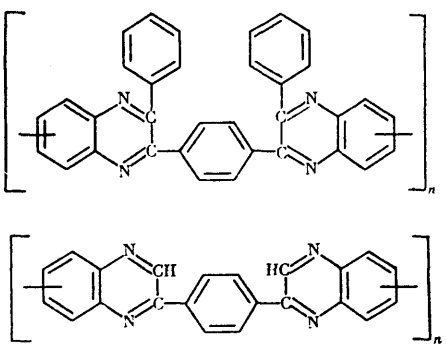
derivatives[57,71,72] in accordance with Scheme 8, are even more thermostable.

Scheme 8

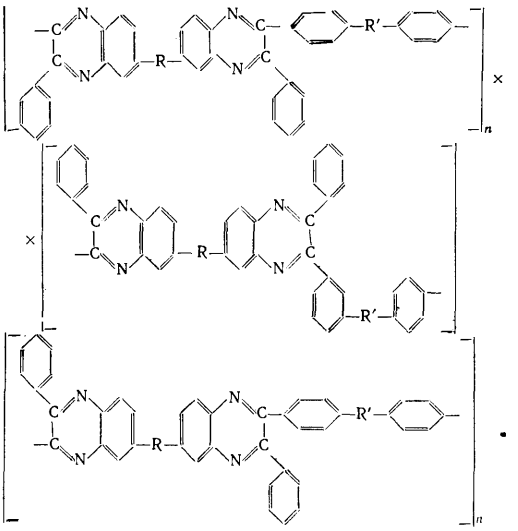


see Scheme 7.

In the series of phenylated polyheteroarylenes these polymers have attracted most attention. A number of careful reviews have been devoted to problems of their synthesis, their properties, and the materials based on them[57,71,72]. We shall therefore not analyse these data in detail. We shall only mention that, like polyphenyl-*asym*-triazines, polyphenylquinoxalines are obtained under very mild conditions. Thus, the polycyclocondensation is carried out at room temperature in phenolic solvents or in chlorinated hydrocarbons. The ease of formation of the quinoxaline ring is responsible for the almost complete absence of uncyclised fragments from these polymers, which, in combination with the high stability of individual heterocyclic compounds of this type, determines the high thermal and chemical stability of polyphenylquinoxalines. These properties of the above systems, combined with their high molecular weights and ready solubility in phenolic solvents, *N*-methyl-2-pyrrolidinone (NP), and chloroform, are responsible for the undoubted practical value of polyphenylquinoxalines, which can be used as binders in reinforced plastics[73,74], adhesives[73], films[72], fibres[72], and other polymeric materials capable of being employed for a long time at 320 °C. In full analogy with polyphenyl-*asym*-triazines, polyphenylquinoxalines also exhibit a higher resistance to thermal oxidation than their unsubstituted analogues. Thus comparison of the thermo-oxidative stabilities of polyphenylquinoxaline based on 3,3'-diaminobenzidine and 1,4-bis(phenylglyoxalyl)benzene and its non-phenylated analogue[75] showed that they lose respectively 6 and 50% of the initial mass at 400 °C in the course of 200 h.



The most significant disadvantage of polyphenylquinoxalines is their high thermoplasticity due to the "isomeric heterounit" structure of these systems: the macromolecules of polyphenylquinoxalines contain isomeric 2,2'-, 3,3'-, and 2,3'-substituted phenylquinoxaline fragments:



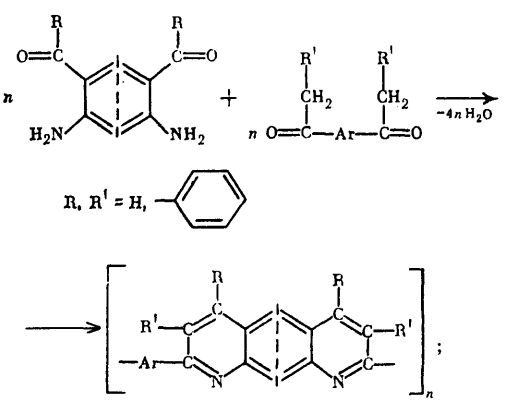
The relative amounts of these fragments in polyphenylquinoxaline macromolecules depend on the nature of the monomers employed. Despite the fact that the interaction of the most nucleophilic amino-groups of bis(*o*-phenylenediamines) with the most electrophilic carbonyl groups of bis(α-diketones) or the interaction of the least nuclephilic amino-groups of bis(*o*-phenylenediamines) with the least electrophilic groups of bis(α-diketones) is most likely, the "isomeric heterounit" structure is characteristic of all polyphenylquinoxalines without exception. As a result, all the known polyphenylquinoxalines proved to be amorphous and the attempts to synthesise ordered systems of this type were unsuccessful[72]. In the search for phenylated polyheteroarylenes free from "isomeric heterounit" structures, a number of investigators turned to polycyclocondensation reactions based on the Friedlaender reaction[76].

IV. PHENYL-SUBSTITUTED POLYHETEROARYLENES OBTAINED BY THE FRIEDLAENDER REACTION

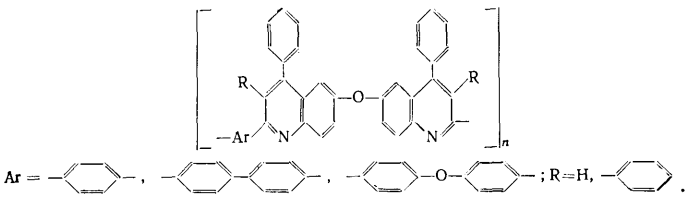
The classical version of this reaction consists in the condensation of *o*-aminocarbonyl compounds with ketomethylene products[76].

A number of phenyl-substituted polymers containing 2,6-quinoline and anthrazoline fragments in the main macromolecular chains have been synthesised by the reaction of diaminodicarbonyl compounds with aromatic diacetyl and diphenylacetyl compounds (Scheme 9).

Scheme 9



In particular the interaction of di(4-amino-3-benzoylphenyl)-ether with bis(α-ketomethylene) compounds in mixtures of *m*-cresol with PPA and P_2O_5 and 130–140 °C yielded a series of poly-2,6-quinolines[77–80] having the general formula

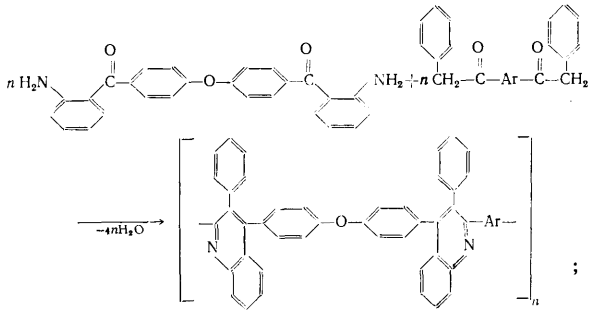


The polymers dissolve in *m*-cresol and chloroform and their intrinsic viscosities are in the range 0.6–4.1 dl g^{-1}. Their glass points are 260–350 °C and their melting points, corresponding to a ~20% degree of crystallinity, are in the range 450–480 °C. The temperatures of the onset of the degradation of poly(2,6-quinolines) are 530–545 °C in air and 530 ° to 570 °C in nitrogen according to DTGA data. Under the conditions of isothermal thermal ageing, polyquinoline based on di(4-acetylphenyl) ether, the least thermostable of the polymers synthesised, did not undergo degradation for 100 h at 300 °C, while after 100 h at 371 °C its mass diminished by 48%.[81]

In the series of polyanthrazolines obtained by the reaction of 4,6-diaminoisophthalaldehyde[80,82,83] and 4,6-dibenzoyl-1,3-phenylenediamine[84] with aromatic diacetyl and diphenacetyl compounds, the greatest interest attaches to systems based on 4,6-dibenzoyl-1,3-phenylenediamine—these are polymers soluble in *m*-cresol, HCOOH, and MP and having η_{log} up to 1.25 dl g^{-1}. According to DTGA data, these polyanthrazolines decompose at 500–550 °C in air and at 530–600 °C in an inert medium.

Poly(2,4-quinolines), which are isomeric with the poly(2,6-quinolines) described above, have been obtained by the reaction of di[4-(2-aminobenzoyl)phenyl] ether with diphenacetyl monomers[85] in accordance with Scheme 10.

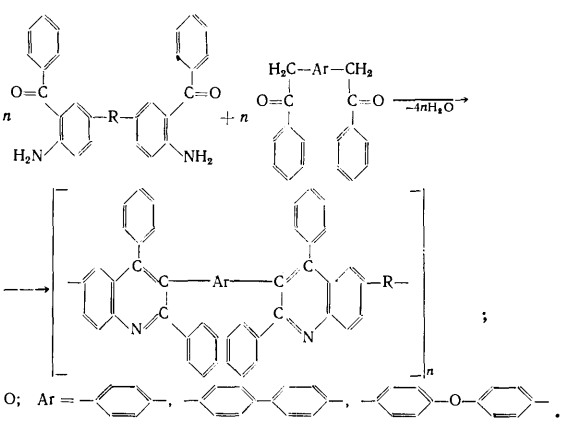
Scheme 10



They are soluble in *m*-cresol and have intrinsic viscosities of 0.26–0.57 in this solvent.

When aromatic diacetyl and diphenacetyl compounds are replaced by diphenacyl monomers of the type of 4,4'-diphenacylbiphenyl, di(4-phenacylphenyl) ether, and 1,4-diphenacylbenzene and on interaction of these products with di(4-amino-3-benzoylphenyl) ether and 4,4'-diamino-3,3'-dibenzoylbiphenyl, phenylated poly(3,6-quinolines) were obtained[86] (Scheme 11).

Scheme 11



Like the phenylated polyquinolines examined above, these polymers are soluble in *m*-cresol, chloroform, and tetrachloroethane and have intrinsic viscosities of 0.5–3.6. Their thermal characteristics are comparable to those of the polyquinolines considered above. Overall, phenyl-substituted polyquinolines and polyanthrazolines have higher softening temperature than polyphenylquinoxalines, but in this case the introduction of phenyl groups significantly increases the thermoplasticity of polyheteroarylenes.

Yet another group of reactions which lead to extensive possibilities for the synthesis of phenyl-substituted polyheteroarylenes consist of modified reductive polyheterocyclisation processes[87].

V. PHENYL-SUBSTITUTED POLYHETEROARYLENES OBTAINED BY A MODIFIED REDUCTIVE POLYHETEROCYCLISATION REACTION

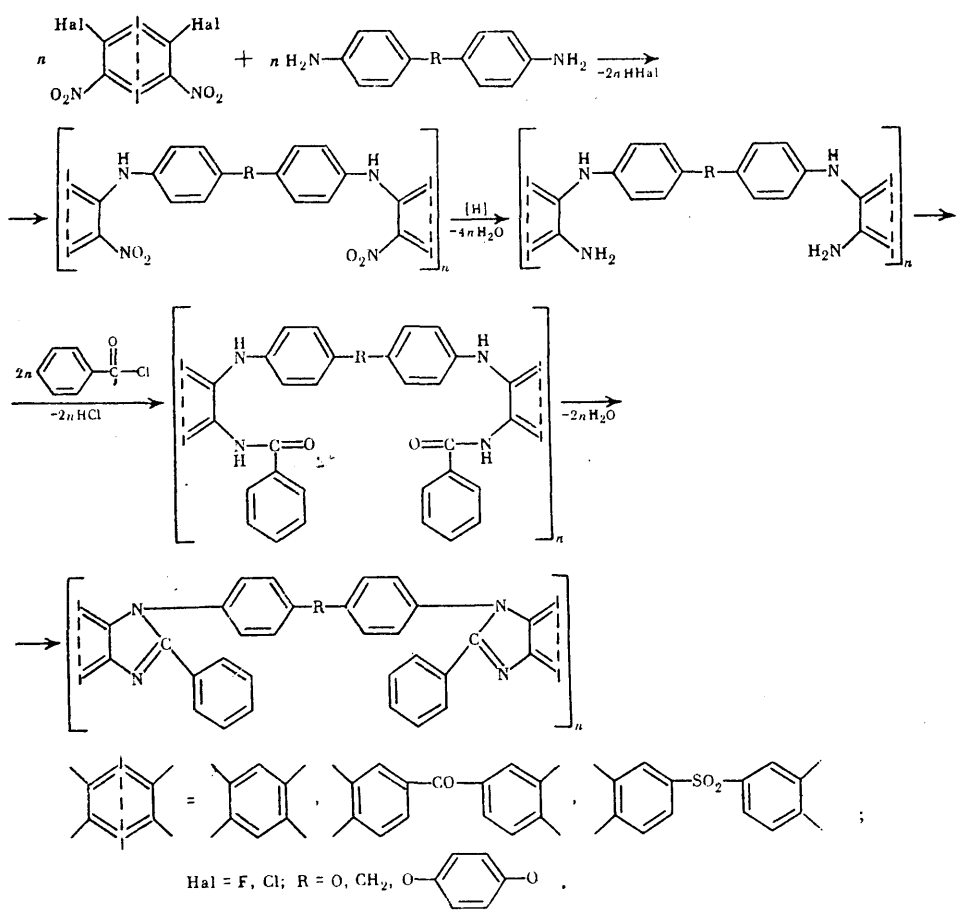
These processes were used successfully for the first time to synthesise *C*-phenyl-substituted polybenzimidazoles, including the interaction of activated bis(*o*-nitro)halogenoarylenes with reactive aromatic diamines[88–94], the reduction of the nitro-groups in the resulting poly(*o*-nitro)amines to the amino-groups[88–92,95], the benzoylation of the latter[88–92,95], and catalytic polycyclisation of the poly(*o*-benzamido)amines formed to poly(*C*-phenyl)benzimidazoles[88–92,96] (Scheme 12).

Such polyphenylbenzimidazole are most usefully synthesised in a single-stage process, i.e. without isolation of the intermediate polymeric structures[88–92], in MP and using as a source of hydrogen and as a polycyclisation catalyst the hydrogen halide evolved as a side product in combination with metals. The employment of a catalyst makes it possible to carry out this process at relatively low temperatures (160–170 °C), eliminating thereby the risk of all possible secondary cross-linking degradation, etc. reactions.

In the series of poly(*C*-phenyl)benzimidazoles, polymers based on di(4-chloro-3-nitrophenyl) sulphone and di(4-aminophenyl) ether or di(4-aminophenyl)methane—readily available and at the same time reactive compounds— are of greatest interest. These polymers have high viscosities, are readily soluble in phenols and amide solvents, and have higher thermal stabilities than the poly(*N*-phenyl)benzimidazoles, which are similar to them in structure (see above).

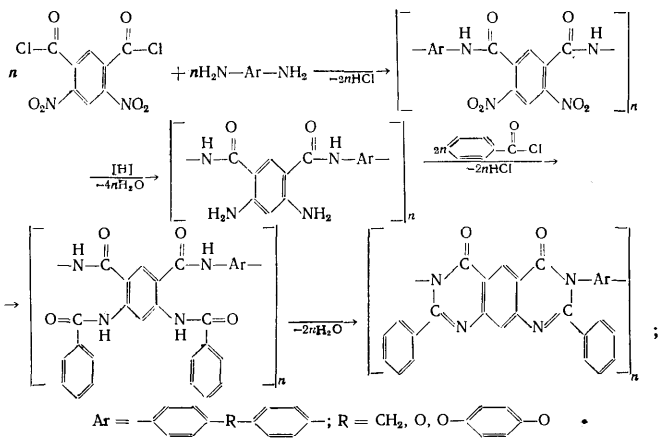
High quality carbon plastics, capable of being used for a long time at 250–300 °C, have been obtained from these polymers[87]. A significant disadvantage of these systems is their low softening temperatures (300–320 °C), which are responsible for their thermoplasticity at elevated temperatures.

Scheme 12



Somewhat higher softening temperatures are characteristic of phenylated polyquinazolinones obtained by the method of modified reductive polyheterocyclisation[97,98], involving the interaction of the dichloride of 4,6-dinitroisophthalic acid with activated aromatic diamines, the reduction of the *o*-nitro-substituents in the resulting polyamides to the amino-groups, benzoylation of the latter, and catalytic cyclisation of the poly(*o*-benzimido)amides formed (Scheme 13).

Scheme 13



The poly(2-phenyl)quinazolinones obtained in this way do not contain unreduced nitro-groups and uncyclised fragments according to the infrared spectroscopic data for the polymers and model compounds. The polymers synthesised are soluble at room temperature in strong acids and phenols and on heating in dipolar and aprotic solvents. The viscosities η_{int} of poly(2-phenyl)quinazolinones are 1.02–1.21 dl g^{-1}, which makes it possible to obtain from these systems strong ($\sigma \leq 1200$ kg cm^{-2}) and fairly elastic ($\varepsilon \geq 12\%$) films. According to DTGA data and the results of isothermal thermogravimetric analysis (ITGA), the thermal stability of these polymers is comparable to that of identical systems obtained by the usual (see above) method[26].

The properties of phenylated and unsubstituted polyheteroarylenes have been by no means compared in all the systems examined above. However, analysis of the available data and systematic arrangement of the results scattered throughout the literature show that in the vast majority of cases the introduction of phenyl substituents into polyheteroarylenes leads to the following results:

1) the improvement of the solubility of polyheteroarylenes in organic solvents;

2) an increase of the resistance of polyheteroarylenes to thermo-oxidative degradation;

3) a decrease of the softening temperatures and hence an increase of the thermoplasticity of polyheteroarylenes.

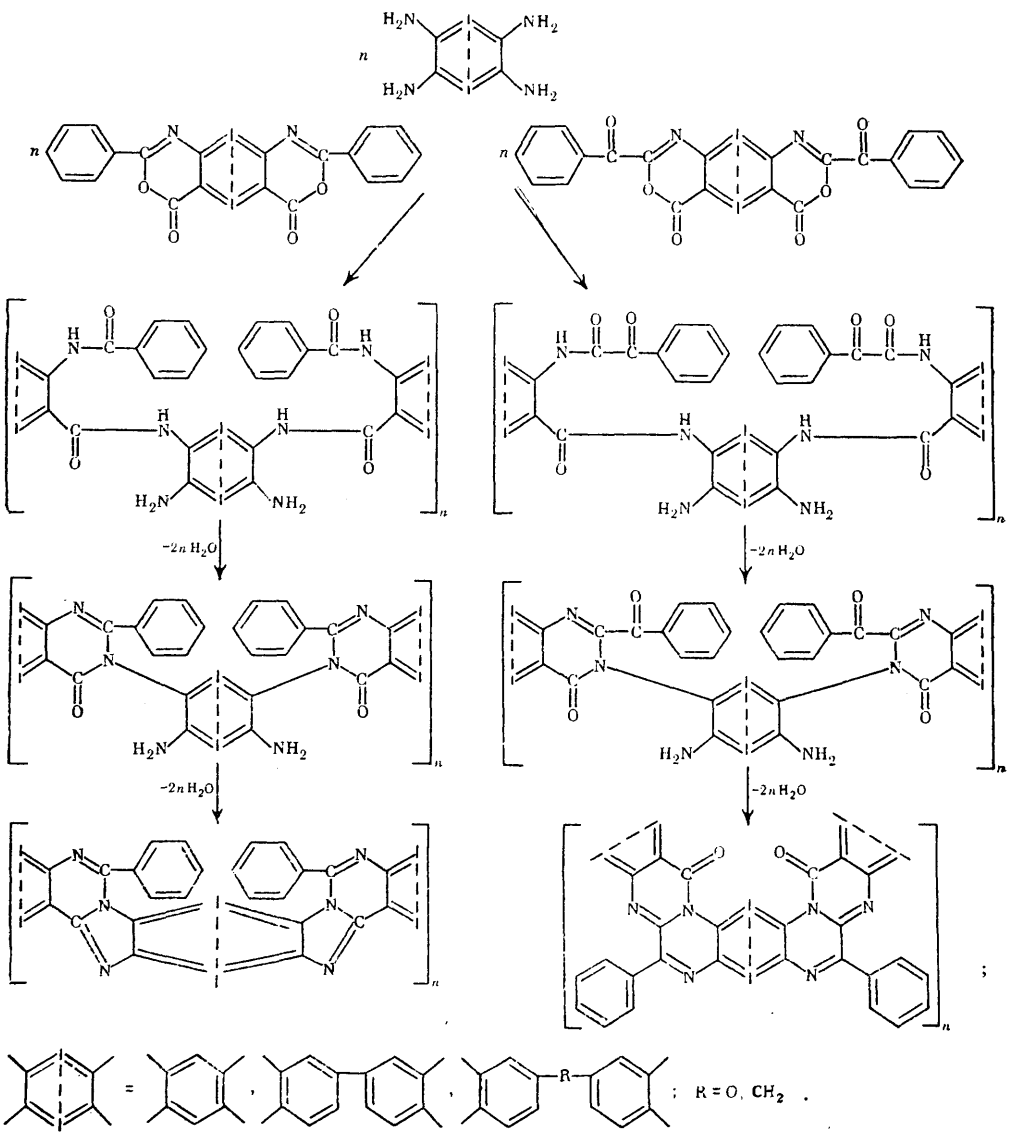
The latter factor facilitates the conversion of polyheteroarylenes into articles, but it limits the temperature ranges in which materials based on polyheteroarylenes can be used. As

a result, the synthesis of phenylated ladder polyheteroarylenes, i.e. systems containing highly condensed aromatic heterocycles in the main chains of the macromolecules, have become one of the most vigorously developing fields in the chemistry of phenyl-substituted polyheteroarylenes[99–101].

VI. PHENYLATED LADDER POLYHETEROARYLENES

The use by Hedberg et al. of aromatic tetra-amines with condensed rings, namely 2,3,7,8-tetra-aminodibenzofuran, 2,3,7,8-tetra-aminophenazine, 1,2,5,6-tetraminoanthraquinone, 2,3,11,12-tetra-aminodiquinoxalino[2,3-*e*: 2′,3′-1]pyrene, and 2,3,8,9-tetra-aminodiquinoxalino[2,3-*e*: 2′,3′-1]cyclopentanepentone for the synthesis of polyphenylquinoxalines[102] led to the formation of polymers soluble in *m*-cresol and at the same time having glass points exceeding 400 °C. Other examples of the synthesis of phenylated ladder polyheteroarylenes are reactions involving the formation of polyphenylquinoxalinoquinazolines[103] and polyphenylbenzimidazoquinazolines[104–106] by the reaction of aromatic bis(*o*-phenylenediamines) with bis(2-phenylbenzoxazin-4-ones) and 6,6′-(2-benzoylbenzoxazin-4-one) in accordance with Scheme 14.

Scheme 14

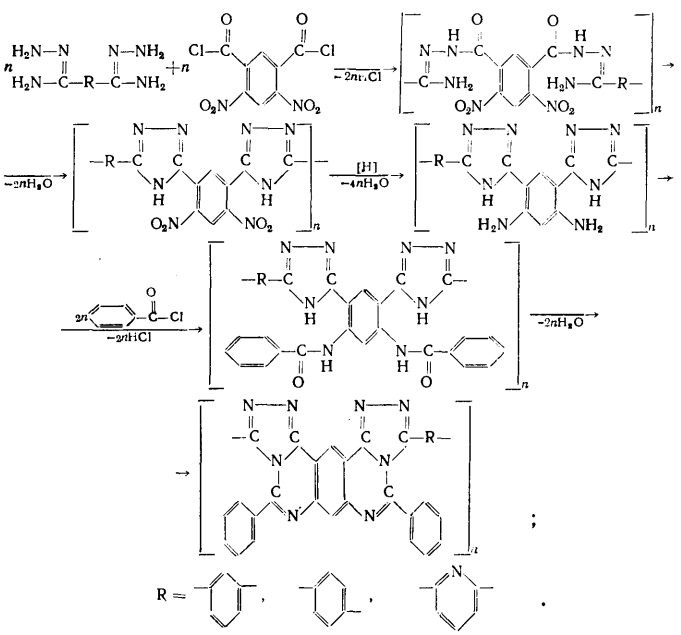


These reactions have been carried out in the melt, in phenolic solvents, or in PPA at elevated temperatures and led directly to the required polymeric structures without the isolation of intermediate systems. The polymers were soluble in acid and phenolic solvents and had a comparatively high thermal stability and heat resistance, but their viscosities (η_{int} up to 0.85) were insufficient to permit the preparation on their basis of materials with acceptable deformation-strength properties.

A number of phenylated ladder polyheteroarylenes have been obtained by the methods of modified and combined reductive polyheterocyclisation[87].

Phenylated polybenzo[di(*S*-triazolopyrimidines)], isomeric with previously known polymers, were obtained in the reaction of the dichloride of 4,6-dinitroisophthalic acid with the bisamidrazones of dicarboxylic acids and in the subsequent reactions of the resulting poly(*o*-nitro)aroylamidrazones[107, 108,109,110] (Scheme 15).

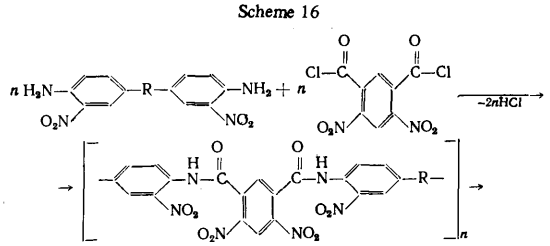
Scheme 15

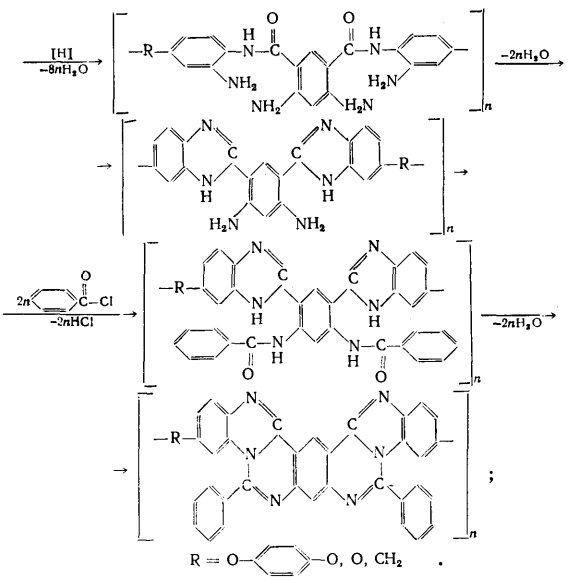


The presence of phenyl side groups and the relatively mild conditions of the polycyclisation processes are responsible for the solubility of the resulting polymers in acid solvents (H_2SO_4 and CF_3COOH) and the 3 : 1 trichloroethane (TCE)–phenol mixture and for their partial solubility in hot MP. A comparative study of the thermal stabilities of polybenzo[di-(*S*-triazolopyrimidines)], synthesised by modified reductive polyheterocyclisation and by the two-stage method[109,110], showed that these systems are comparable.

When various bis(*o*-nitroanilines) were used as the comonomers of the dichloride of 4,6-dinitroisophthalic acid, phenyl-substituted polybenzo[di(pyrimidinobenzimidazoles)] were obtained[111,112] (Scheme 16).

Scheme 16





Phenyl substituents combined with mild conditions of the polycyclisation processes are responsible for the solubility of the polymers in the 3 : 1 TCE–phenol mixture, H_2SO_4, and CF_3COOH. The thermal stabilities of polybenzo[di(pyrimidinobenzimidazoles)] obtained by reductive polyheterocyclisation are comparable under ITGA conditions with those of polymers obtained by the two-stage method[109,110].

The softening temperature of polybenzo[di(*S*-triazolopyrimidines)] and polybenzo[di(pyrimidinobenzimidazoles)] are in the range 350–420 °C, depending on the structure of the polymers.

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The introduction of phenyl substituents into polyheteroarylenes constitutes a reliable and effective method of increasing the solubility of the polymers and their overall capacity for being converted into articles. By varying the structure of the main macromolecular chains, it is possible to obtain phenyl-substituted polyheteroarylenes with softening temperatures from 250° to 400 °C and to generate a wide assortment of polymers of interest for the preparation of thermostable polymeric materials.

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Thermophysical Properties of Irradiated Polymers

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The effect of ionising radiation on the specific heat, thermal conductivity, thermal diffusivity, and density of partially crystalline (polyethylene, polypropylene, polytetrafluoro-ethylene) and of amorphous polymers (polystyrene, poly(methyl methacrylate)) is discussed. Analytical models of the mechanism of heat conduction, and the development of anisotropic thermal conductivity in amorphous polymers, are examined. The influence of ionising radiation on the thermophysical properties of composite materials is analysed. 79 references.

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I. INTRODUCTION

Information about the influence of ionising radiation on the thermophysical characteristics of polymeric materials is important, for two reasons. Firstly, because the thermal state of constructional materials used in the new technologies in the presence of powerful ionising radiations is determined by the thermal constants of these materials, and secondly because the structure of the polymer can be inferred from the temperature and dose dependence of the thermal conductivity and (even more directly) of the specific heat. Thus information on the phonon mechanism of energy transfer in polymers and on the phase composition of the partially crystallised materials can be obtained from the changes in thermal conductivity λ. Measurements of the specific heat c_p of solid polymers have been used to study molecular mobility, relaxation processes, phase transitions, etc.; the high precision of calorimetric methods over a wide temperature range ensures that the information is unambiguous.

In spite of the importance of the influence of ionising radiation on the thermophysical properties of polymers, very few experimental data have been published on this topic (compared, for example, with the number of data on radiation effects on the mechanical and dielectric properties of the same materials). This may be due to the practical difficulty of measuring λ, c_p, and the thermal diffusivity coefficient a, and to the shortage of apparatus offering adequate precision. Another reason is that marked changes in thermophysical properties are observed only for very high absorbed doses of radiation (up to tens of Mrad). This causes practical difficulties and necessitates the use of fairly powerful radiation sources.

Results so far reported indicate a large difference between the radiation effects in crystalline and in amorphous polymers. Published data on the effects of ionising radiation on the specific heat c_p, the thermal conductivity λ, the density ρ, the degree of crystallinity x, and the melting point will therefore be reviewed separately for partially crystalline and for amorphous polymers.

II. PARTIALLY CRYSTALLINE POLYMERS

There are two important differences between simple solids and solid linear polymers: the chemical structure of the polymers is far more complex, and their physical structure is often metastable, and variable for a given chemical structure. This makes the thermal properties of the polymers a function of the thermal history of the sample, and also of the heating rate (in dynamic experiments). Because of the strong influence of the thermal history on the structure of polymers, both amorphous and crystalline, most of the discrepancies in published data on radiation interaction with polymers can be explained by differences in morphology between the different samples.

1. Polyethylene

a) *Specific heat of polyethylene.* Though the specific heat of polyethylene (PE) has been studied over a wide range of temperature in many laboratories (see, for example, reviews in Refs.1 and 2), relatively little work has been done on the effect of irradiation on c_p[3-5]. Radiation effects on c_p have been studied only above 20 °C. Thus, PE of PE-500 grade with an initial density of 915 kg m^{-3} and c_p = 1.91 kJ kg^{-1} K^{-1} has been irradiated[4] with γ quanta from a ^{60}Co source up to a dose of 6.1 Mrad. The irradiation temperature T_i and the measurement temperature T_m were both ~ 30 °C. As the dose was increased, c_p fell monotonically to 1.45 kJ kg^{-1} K^{-1}. This decrease in specific heat was ascribed[4] to the formation of cross-links between the linear macromolecules, which lowers the number of internal degrees of freedom.

High-pressure PE (c_p = 918 kg m^{-3}) was irradiated[5] in air with ^{60}Co γ quanta at a dose rate of 7.5 rad s^{-1} and T_i = 40 °C to give a range of absorbed dose up to 50 Mrad. Each sample was subjected to at least two heating runs (heating rate ~ 1K min^{-1}). The temperature dependence of c_p between 20 and 70 °C was linear for the PE samples which had not

been irradiated. Beyond this range the increase of c_p becomes much steeper, suggesting the onset of melting of the crystalline phase. The melting point (T_f) was found to be 110 °C. In the range 110–113 °C a large exothermic effect was observed, and c_p fell steeply from ~ 11.0 to ~ 1.6 kJ kg^{-1} K^{-1}. Further heating to 120 °C increased c_p to 2.5 kJ kg^{-1} K^{-1}. Repeated heating of the same sample (using the cycle: first heating to 90 °C, cooling, second heating to 140 °C) lowers the melting peak (observed in the second heating period) by 2 K. In the region of 95 °C a pre-melting effect occurs during the second heating: a sharp increase in c_p from 3.7 to 6.5 kJ kg^{-1} K^{-1} followed by a decrease to 5.1 kJ kg^{-1} K^{-1}. Very similar effects are observed for c_p in irradiated samples (Fig. 1a–1c). The position of the c_p maximum on the successive curves of the repeated heating cycle coincides with the maximum heating temperature of the preceding run. This phenomenon persists until all the crystals initially present in the sample have been melted.

A large number of melting peaks on the curve of c_p against T for PE was reported also in Ref. 6. An increase in the absorbed dose caused a marked decrease in the height of the main melting peak: at 30 Mrad the peak became diffuse, and at 50 Mrad it disappeared completely. The pre-melting peaks disappeared at doses greater than 10 Mrad, and the 110–120 °C exothermic effects disappeared at doses greater than 5 Mrad. At the same time as the heat of melting, the melting point T_f also decreases (as shown by the coordinate of the specific heat maximum).

The initial model used to explain the changes in thermophysical properties of partially crystalline polymers is usually the classical two-phase model[7–9], even though the structure of polyethylene is quite different from that of an ideal two-phase system, and the presence of marked relaxation processes in PE (pre-melting region) is well recognised. Godovskii[10] has criticised the hypothesis of a crystalline phase embedded in an amorphous matrix.

According to published data on the temperature dependence of c_p, the melting processes can extend over the temperature region 80–113 °C. This is evidence of a wide range of crystallite sizes, each crystalline formation having its own melting point. The "boundary melting" effect discussed in Ref. 11 may also be partly responsible for the wide melting range of these materials.

The nature of the non-equilibrium melting process is determined by the previous history of the sample: the situation is further complicated by the possibility of new partial crystallisation at a stage during the melting process when the temperature is quite high and the relative amount of crystalline phase is substantially decreased. This possibility is confirmed by the exothermic effects in the pre-melting region of both the irradiated and the non-irradiated PE.[5] When the system reaches a high enough temperature all the crystals suddenly melt. A similar phenomenon was observed in a study[12] of the thermodynamic behaviour of PE single crystals. The gradual flattening out of the $c_p = f(T)$ curve with increase in the absorbed dose is obviously caused by a

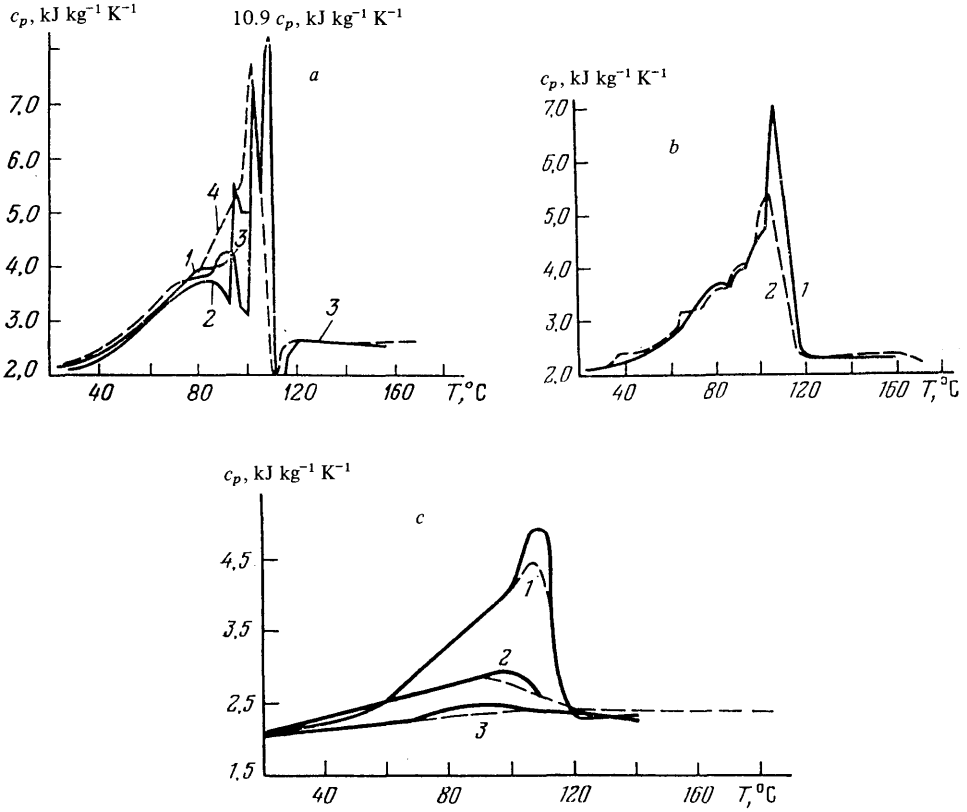


Figure 1. Temperature dependence of the specific heat of high-pressure polyethylene. (*a*) 2 Mrad dose, heated to different temperature: 1) 90, 2) 100, 3) 150, 4) 160 °C. (*b*) 5 Mrad dose: 1) first heating, 2) second heating. (*c*) different doses: 1) 10, 2) 30, 3) 50 Mrad (full lines denote first heating, broken lines second heating[5]).

decrease in crystallinity. The characteristic decrease in T_f and in the c_p maximum observed in all the samples subjected to heating cycles may be due to a decrease in size of the crystallites formed in the polyethylene during the cooling period.

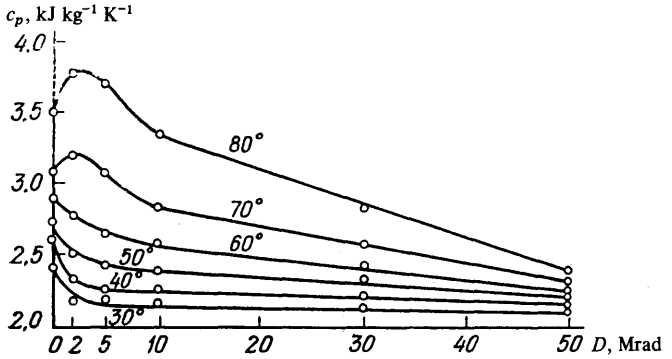


Figure 2. Dependence of the specific heat of high-pressure polyethylene on the dose of radiation for different measurement temperatures[5].

Plots of c_p against the absorbed dose are shown in Fig.2 for different measurement temperatures T_m.[5] In the 30–50 °C temperature range the parameter c_p decreases monotonically as the dose increases, but at and above 70 °C it goes through a maximum at D = 2 Mrad. Since c_p is higher for an amorphous than for a crystalline PE phase[13], the decrease in crystallinity produced by the irradiation should make the specific heat vary in the same sense as the dose. However, when the PE molecules become cross-linked the increased rigidity of the system (or, in other words, the loss of internal degrees of freedom) causes c_p to decrease. Evidently, at 30–50 °C the cross-linking process predominates over the amorphisation process for the whole range of doses. At T_m = 70 °C (and above) the intensification of the melting process increases the relative amount of amorphous phase, and the specific heat can therefore increase for doses up to ~ 2 Mrad, but at higher levels of cross-linking c_p begins to decrease with increasing dose.

Some of the published data on the effect of radiation-induced cross-linking on T_f in PE crystals are contradictory. Both a decrease in T_f with increase of dose[14] and an almost constant T_f[15] have been reported. Ushakov and co-workers[16] irradiated low-pressure PE samples (LPP) in the solid state (T_i = 45–50 °C) and as melts (T_i = 130–140 °C). In the solid samples T_f fell from 135 to 118 °C for a dose of ~ 5.5 Mrad, rising again to 124 °C at a dose of 11 Mrad, whereas irradiation in the melt lowered T_f to 50 °C even at a dose of 5.5–6 Mrad. For high-pressure polyethylene (HPP) at T_i = 45–50 °C the melting point T_f goes through a minimum as the dose increases (~ 107 °C for D = 6 Mrad), and then rises again to its original value (113 °C for D = 11 Mrad). As was stated above, T_f for HPP has been found[5] to decrease from 110 to 106 °C as the dose is increased to D = 10 Mrad. The maximum T_f value for the diffuse endothermic peak at a dose of 30 Mrad was 100 °C.

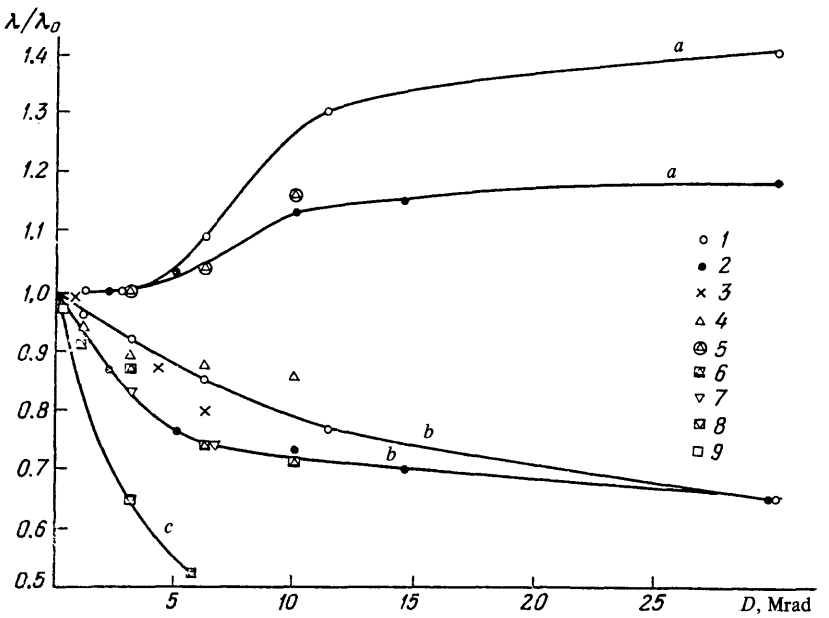


Figure 3. Relative thermal conductivity of polyethylene as a function of dose of radiation for different measurement temperatures [30 °C (*a*), 150 °C (*b*), and −150 °C (*c*)]. HPP: 1) from Ref.17, 2) from Ref.19, 3) from Ref.4, 4) from Ref.18, 5) from Ref.18, 6) from Ref.18; LPP: 7) from Ref.18, 8) from Ref.18, 9) from Ref.9.

Radiation-induced cross-linking causes a decrease in the degree of crystallinity and in the size of the crystallites, which lowers T_f, but on the other hand it also imposes some molecular order within each crystal, as shown by measurements of double refraction in spherulites of irradiated PE.[16] This local ordering effect causes an increase in T_f. As a result, the real behaviour of T_f in particular samples of PE becomes a function of the initial crystallinity and of the irradiation temperature.

The decrease in T_f to 105 °C in the second heating run (mentioned above) is practically constant for doses up to 10 Mrad.[5] PE has a "memory", and when the sample is cooled new crystals are formed on the original sites, but these are smaller as a result of cross-linking in the crystalline phase and they melt at lower temperatures. Since the thermal conditions for recrystallisation are approximately the same in different samples, we can expect constant values of the crystallite size and therefore also of T_f.

b) Thermal conductivity and density of polyethylene. As in the case of the specific heat, the effect of irradiation on the thermal conductivity λ of polyethylene is largely determined by the irradiation conditions and by the initial crystallinity of the polymer. Studies of radiation effects on λ in PE are mentioned in several papers[3,4,9,17-19]. Since λ is higher in a crystalline than in an amorphous phase (the mean free path of phonons being longer in crystals than in amorphous phases, where it is limited by the disordered arrangement of the atoms to a value of the same order as the interatomic distance) we can expect a decrease in λ in irradiated polyethylene. But at the same time the cross-linking of the molecular chains increases the packing density of the macromolecules, thus increasing the effective mean free path of the phonons, i.e. increasing λ. As a result, the behaviour of the thermal conductivity in irradiated samples depends on the relative magnitude of these competing processes.

Data on the relative changes in λ for HPP and LPP as a function of dose of radiation are shown in Fig.3. Some workers[4,9] irradiated their samples with γ quanta at T_i = 30 °C, others[18] used an electron beam (E = 1 MeV) giving a dose rate of 1.7 krad s^{-1} and absorbed doses up to 10 Mrad. In Refs.17 and 19 mixed radiation from a reactor was used at T_i = 80 °C. In Fig.3 curves *a* and *b* are drawn through the experimental points of Refs.17 and 19 for T_m values of 150 and 30 °C respectively, and curve *c* is drawn through the points of Ref.9 (T_m = −150 °C, LPP). The difference between the results from Refs.17 and 19 may be due to differences in the crystallinity of the initial samples. In the range of measurement temperatures (T_m) from −150 to 80 °C the λ value of polyethylene decreases as the absorbed dose is increased to ~ 20 Mrad (see Fig.4 below), indicating amorphisation of the polymer by the radiation. A gradually increasing contribution from radiation-induced cross-linking effects eventually stops the changes in λ, assisted by the increasing contribution from degradation processes. At the higher measurement temperatures ($T_m > T_f$) the crystallinity of the sample is low (or zero). Therefore the changes in λ due to radiation-induced cross-linking become more marked. However, the processes responsible for changes in λ are gradually inhibited by polymer degradation effects.

The influence of dose on λ at $T < T_f$ is more marked below the glass transition temperature (T_g) than in the region $T_g < T < T_f$. From the standpoint of the two-phase model this is explained by the strong temperature dependence of the thermal conductivity of the crystalline phase ($\lambda_{cr} \propto 1/T$) as compared to that of the amorphous phase (λ_a). As a result, the difference $\lambda_{cr} - \lambda_a$ increases sharply as the temperature falls. Under these conditions the effect of the dose of radiation, which lowers the crystallinity, becomes much stronger.

The effect of the irradiation temperature T_i on the changes in λ in polyethylene is shown in Fig.4, using data from Ref.19. We should note that a visual examination of the cross-section of samples irradiated at T_i = 80 °C (dose rate P = 200 rad s^{-1}) revealed small pores when the dose exceeded 2 Mrad, whilst at higher doses even cracks were observed. The number and size of these defects increased with the dose, suggesting gas evolution during irradiation. At T_i = 30 °C (P = 13 rad s^{-1}) the gaseous hydrolysis products can diffuse into the surroundings without producing large internal stresses. It is clear from Fig.4 that though the curves for two series of measurements at different irradiation temperatures have the same shape, the absolute values of λ are 15–20% lower for T_i = 80 °C than for T_i = 30 °C. This is due to differences in crystallinity and porosity between the samples. As the temperature of the sample increases, the degree of crystallinity decreases, and the thermal resistance of the pores decreases because of the increasing contribution from radiative heat transfer[20]. The net result is a decrease in the difference between the λ values for two series of experiments as a function of dose for T_i above 80 °C. Thus for T_i = 30 °C and a dose of 23 Mrad the difference between the λ values is 19%, and for T_i = 100 °C it is 8%.

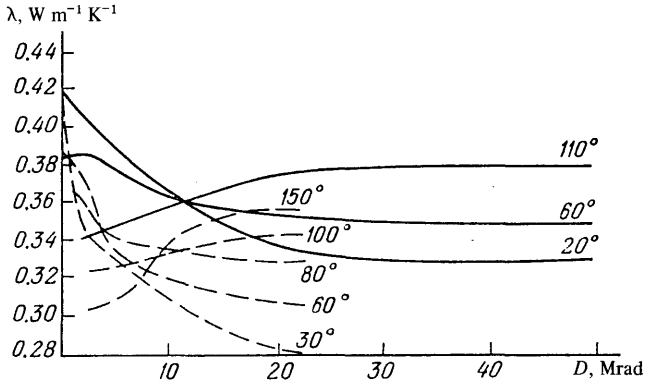


Figure 4. Dependence of the thermal conductivity of high-pressure polyethylene on the dose of radiation for different measurement temperatures (full curves for T_i = 30 °C, broken curves for T_i = 80 °C[19]).

A high initial crystallinity results in a steeper dose dependence of the λ value of polyethylene. Thus[9] even at a dose of 0.3 Mrad the λ value of polyethylene of density ρ = 947 kg m^{-3} is decreased by 3%. The difference in the behaviour of λ between HPP and LPP is clearly shown in Fig.3.

The thermal conductivity of polymers is known to be closely correlated with their density, since an increase in density causes an increase in the phonon mean free path, and hence in λ. Evidently, changes in density induced by radiation should also depend on the irradiation temperature. It has been shown[21] that irradiation of HPP with doses of up to 20 Mrad produces a minimum on the $\rho = f(D)$ curve at D = 5 Mrad (T_m = 20 °C), while the density increases monotonically from ρ = 780 to ρ = 890 kg m^{-3} at D = 20 Mrad (T_m = 150 °C). Data[17,19,22] on the effect of irradiation temperature (T_i) on the shape of the $\rho = f(D)$ curves for HPP are shown in Fig.5. In every case the temperature of the sample during the measurement (T_m) was 20 °C.

Analogous results were obtained[23] by using mixed (gamma and neutron) radiation at T_i = 80 °C. In this case the density minimum was obtained at a dose of 4–5 Mrad. On the other hand, measurements for T_i = 30 °C gave a monotonic increase in ρ with dose of radiation[4] from the initial value of 915 kg m^{-3} to 1005 kg m^{-3} for D = 6.1 Mrad.

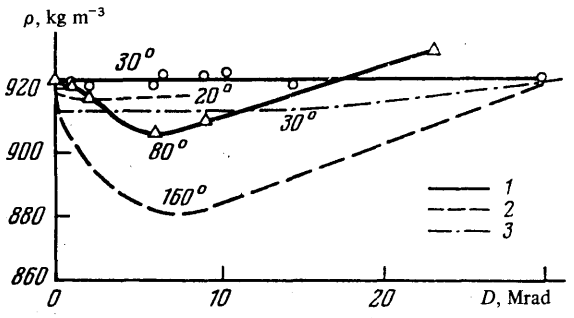


Figure 5. Density of high-pressure polyethylene against dose of radiation for different irradiation temperatures: 1) from Ref.19, 2) from Ref.22, 3) from Ref.17.

The mechanism of the change in density of polyethylene is exactly the same as that described above for the thermal conductivity. For relatively low values of T_i (20–30 °C) the amorphisation of the PE (which causes ρ to decrease, since $\rho_{cr} > \rho_a$) is largely compensated by the radiation-induced cross-linking. Under these conditions ρ either remains constant over a wide range of doses or increases slightly. An increase in T_i causes a large increase in the rate of amorphisation without a proportionate increase in cross-linking. The result is a decrease in ρ for polyethylene irradiated with doses up to 5 Mrad, followed by an increase.

The presence of a minimum on the $\rho = f(D)$ curve for T_i = 160 °C (T_f) is due to partial recrystallisation of the sample during the cooling period after irradiation. A monotonic increase in density with dose of radiation for T_i = 150 °C can be obtained[21] by very slow (near-equilibrium) cooling of the sample after irradiation, or by using a preliminary anneal.

Table 1. Thermal diffusivity of irradiated polyethylene[19].

D, Mrad	$10^7 a$, m^2 s^{-1}			D, Mrad	$10^7 a$, m^2 s^{-1}		
	20° C	40° C	80° C		20° C	40° C	80° C
0	2.00	1.71	1.13	10	1.90	1.88	1.21
2	1.99	1.85	1.15	20	1.74	1.79	1.33
5	1.94	1.91	1.18	30	1.69	1.74	1.41

c) *Thermal diffusivity of polyethylene.* Table 1 gives the thermal diffusivity values (a) of irradiated PE, calculated by the formula $a = \lambda/c\rho$ from the results of Ref.19 for T_i = 30 °C. According to Samoilov[4], radiation-induced changes in the thermal diffusivity of PE measured at $T_m \approx 20$ °C are undetectable for doses up to 6 Mrad. This is not inconsistent with the previous results[19], since the change in a found for the same range of radiation doses with T_m = 20 °C was less than 5%. The dependence of a on the absorbed dose is determined mainly by the behaviour of the thermal conductivity characteristics.

d) *Thermophysical properties of the amorphous phase, and crystallinity of polyethylene.* Our calculations of these properties[24] were based on the two-phase model of PE. Since cross-linking under the influence of radiation occurs mainly in the amorphous phase, the thermophysical characteristics of the crystalline phase were assumed to be constant.

The temperature dependence of the specific heat of the crystalline phase (c_{cr}) and of the amorphous phase (c_a) in non-irradiated PE was calculated as in Ref.8; the corresponding values of λ_{cr} and λ_a have been reported previously[25,7], and also those of ρ_{cr} and ρ_a.[26] The calculations of λ_a were carried out[7] with samples having different initial levels of crystallinity (x). In our experiments[24] changes in x were carried out by irradiation, using published data[5,19,20].

The parameter x was measured[24] either from the specific heat of polyethylene irradiated at T_i = 30 °C or from the density of PE for T_i = 80 °C. The values of $c_{cr} = f(T)$ used in the calculations[24], taken from Refs.7–9, are internally consistent and very reliable.

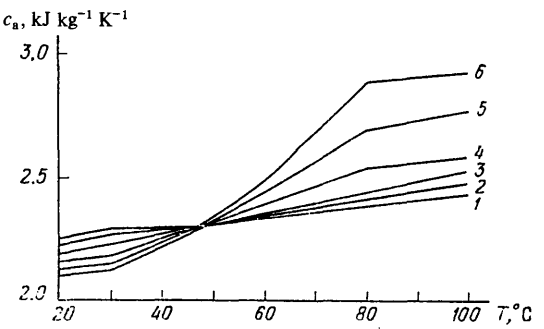


Figure 6. Temperature dependence of the specific heat of the amorphous phase of polyethylene for different doses of radiation[24]: 1) 0, 2) 2, 3) 5, 4) 10, 5) 20, 6) 30 Mrad; T_i = 30 °C.

The method of determining the specific heat c_a of irradiated PE consisted in a linear extrapolation of the experimental plot of c_p for PE samples fully amorphised by irradiation to the value c_a for D = 0.[8] The dose of radiation corresponding to full amorphisation of polyethylene was taken to be 30 Mrad. It was found (Fig.6) that in the range of doses between 0 and 30 Mrad and for T_m less than ~ 50 °C the c_a values decrease with dose as a result of radiation-induced cross-linking (by 10% at T_m = 20 °C). For T_m = 50–100 °C on the other hand the c_a values increase with dose (by 20% at T_m = 100 °C). In this region of temperature the predominant role is played by the decreased rigidity of the amorphous matrix resulting from the breakdown of the crystals.

Exact determination of the degree of crystallinity x of polymers is often difficult. The most accurate (though laborious) method is the calculation of x from calorimetric data, using the expression

$$c = c_a[1 - x(T)] + c_{cr}\, x(T) + \Delta H \partial x/\partial T, \qquad (1)$$

where ΔH is the heat of melting of the polymer. Most workers[8,27] ignore the dependence of x on T and use the simplified expression

$$c = c_a(1 - x) + c_{cr} \cdot x,$$

which can lead to serious errors at high temperatures. Shimchuk and co-workers[28] used Eqn.(1), but they avoided solving the differential equation by making the substitution

$$c = c_{cr}\, x + (1 - x)c_a + b\Delta H$$
$$x = a - b(T - T_f);\ b = -\mathrm{d}x/\mathrm{d}T\ .$$

In the differentiation of the expression for x the non-linear terms were ignored[28], because their effect is appreciable only at high temperatures. Because of these assumptions the melting point of the crystals was incorrectly calculated as 80 °C.

To determine $x = f(D,T)$ we have re-written Eqn.(1) as[24]

$$\frac{\partial x(D,T)}{\partial T} + \frac{1}{\Delta H}[c_a(D,T) - c_{cr}(T)]\, x(D,T) = [c_a(D,T) - c(D,T)]\frac{1}{\Delta H} \qquad (2)$$

with the boundary condition $x = 0$ for $T = T_f = \phi(D)$. The parameter ΔH for PE was found to be 277 J g^{-1} (according to Refs.8 and 29), 275 J g^{-1} (Ref.30), and 271 or 280 ± 9 J g^{-1} (Ref.31). In the solution of Eqn.(2) a value of ΔH = 276 J g^{-1} was used.

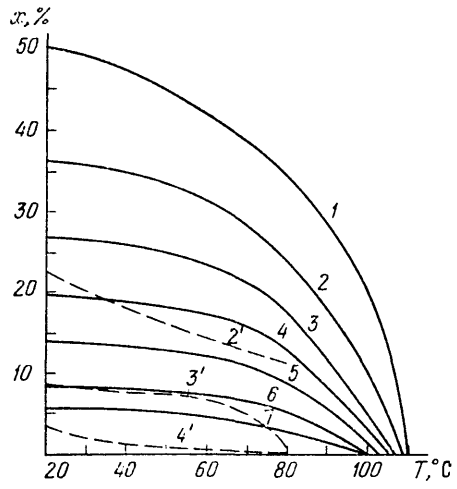


Figure 7. Temperature dependence of the crystallinity of polyethylene for different doses of radiation: 1) 0, 2) and 2') 2, 3) and 3') 5, 4) and 4') 10, 5) 15, 6) 20, 7) 25 Mrad (full lines T_i = 30 °C, broken lines T_i = 80 °C[24]).

The results (Fig.7) of our numerical integration[24] of Eqn.(2) show that the degree of crystallinity of PE decreases at temperatures above T_m = 30 °C (full curves, T_i = 30 °C). The behaviour of x for D = 0 is consistent with earlier results[32,33] and confirms the general validity of our method[24].

The $x = f(D)$ dependence shown in Fig.7 agrees on the whole with the results[21] obtained by Nikitina for 20 °C. The only exception is the dose for full amorphisation, which Nikitina gives as 20 Mrad.

It has been reported[34] that when HPP with an initial crystallinity of 50% is irradiated with a dose of up to 2 krad the x value falls to 33%, rising again to 50% for a dose of 1 Mrad before decreasing once again. The temporary restoration of the crystallinity during irradiation is ascribed to the photochemical breaking of the distorted bonds in the keto groups formed by irradiation in air. It is suggested[34] that in this case some of the units can be accommodated in the crystalline lattice. However, this hypothesis is not confirmed by our results.

The degree of crystallinity can be calculated from the densities ρ or from the specific volumes v of the separate phases: the crystallinity by weight is given by the formula

$$x = \frac{v_a - v}{v_a - v_{cr}} = \frac{\rho_{cr}}{\rho}\frac{\rho - \rho_a}{\rho_{cr} - \rho_a} = \frac{1 - \rho_a/\rho}{1 - \rho_a/\rho_{cr}}$$

and the crystallinity by volume by the formula

$$\gamma = \frac{\rho - \rho_a}{\rho_{cr} - \rho_a} = \frac{\rho}{\rho_a}\, x \qquad (3)$$

Table 2. Density of the amorphous phase of polyethylene.

T_m, °C	ρ_a, kg m^{-3}	
	(Ref.24)	(Ref.26)
20	855	855
40	842	842
60	830	829
80	818	817

The density of the amorphous phase ρ_a can be determined by extrapolating to room temperature the ρ values measured at $T > T_f$. Ross[23] obtained a ρ_a value of 877 kg m^{-3} at T_m = 20 °C for HPP irradiated to D = 4 Mrad by extrapolation to D = 0, and 853 kg m^{-3} for non-irradiated HPP. By using Eqn.(3) for T_i = 30 °C, and data on crystallinity obtained in Ref.24, we have calculated[24] the $\rho_a = f(D,T)$ dependence (see Fig.8, full lines). Over the whole range of radiation doses (up to 30 Mrad) ρ_a increases with dose as a result of radiation-induced cross-linking. The increment $\Delta\rho_a$ for a dose of 30 Mrad is 8–10%. In the range of T_m = 20–80 °C the parameter ρ_a decreases monotonically with temperature for all doses of radiation, and the temperature coefficient is practically independent of the dose (~ 6 × 10^{-4} K^{-1}). The ρ_a value for non-irradiated PE agrees very well with published data[26] (see Table 2). The results of Ross mentioned above[23] on the ρ_a value of irradiated HPP are also consistent with our calculation[24], confirming the validity of the proposed method for calculating crystallinity and for determining the $c_a(D)$ relationship[24].

To calculate the ρ_a values of HPP irradiated at T_i = 80 °C we used[24] a linear extrapolation of the experimental densities ρ for D = 10–15 Mrad (corresponding to complete amorphisation of the PE) to D = 0. The ρ_a values obtained in this way (Fig.8, broken curves) are higher than the ρ_a values for T_i = 30 °C, the largest difference corresponding to the measurement temperature T_m = 80 °C. This dependence of the density ρ_a on the irradiation temperature is probably due

to an increase in the yield of radiation-induced cross-links, which has been found[35,36] to increase four-fold as the irradiation temperature is varied from −196 to +73 °C.

By combining these values of ρ_a with Eqn.(3) we calculated the degrees of crystallinity $x(D,T)$ for T_i = 80 °C (shown in Fig.7 as broken curves). As could have been expected, the crystallinity of PE decreases steeply as the irradiation temperature is increased.

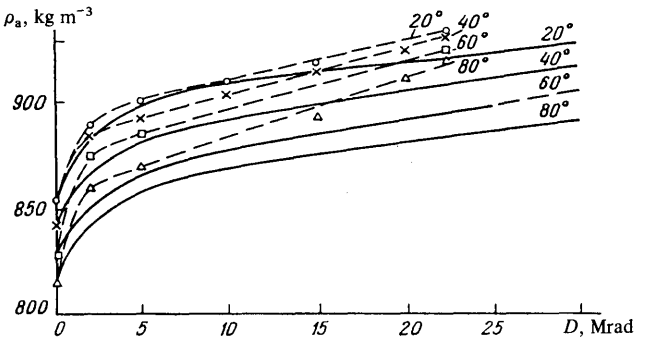


Figure 8. Density of the amorphous phase of polyethylene against dose of radiation for different measurement temperatures: full lines for T_i = 30 °C, broken lines for T_i = 80 °C[24].

The thermal conductivity λ_a of the amorphous phase of non-irradiated PE has been discussed in many papers[7,37-40], usually in terms of the two-phase Maxwell–Eucken model:

$$\lambda = \frac{2\lambda_a + \lambda_{cr} + 2\gamma(\lambda_{cr} - \lambda_a)}{2\lambda_a + \lambda_{cr} - \gamma(\lambda_{cr} - \lambda_a)}\lambda_a \quad . \qquad (4)$$

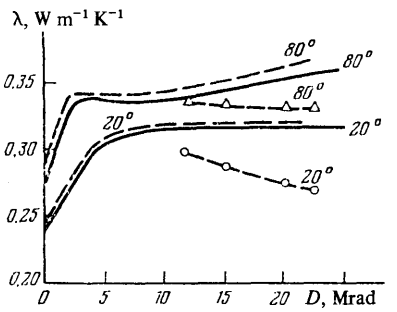


Figure 9. Thermal conductivity of the amorphous phase of polyethylene against dose of radiation for different measurement temperatures: full lines for T_i = 30 °C, broken lines for T_i = 80 °C. The broken lines with experimental points are for samples containing pores (T_i = 80 °C)[24].

Some workers[41,42] have used the Bruggeman model[43] and the Cheng–Vachon model[44] to determine the thermal conductivity of two-phase solid systems. It has been shown[7] that λ_a increases with temperature up to the glass transition temperature T_g = −20 °C, and decreases slightly at higher temperatures. This type of temperature dependence of λ_a has been explained by postulating[7] a constant value of the volume crystallinity γ. However, the same type of $\lambda_a = f(T)$ dependence is obtained[37] even allowing for the temperature dependence of γ. A different model[9] of the disposition of the crystallites in the amorphous matrix gave λ_a values lower than those of Ref.7 without affecting the shape of the temperature dependence. The decrease of λ_a with increase of temperature above T_g is explained[39] in terms of the increased free volume of the molecules. A proposed[40] generalised relationship between λ_a and the fractional free volume for amorphous polymers at temperatures above T_g implies a decrease in λ_a with increase in temperature (we note that data from Ref.7 were used for PE in these calculations). On the other hand, Hattory found[38] that λ_a for PE increases monotonically in the range 20–100 °C, and he explained this by postulating excitation of micro-Brownian motion of the polymer molecules at temperatures above T_g. Similar conclusions were reached by other workers[45,46].

We have calculated[24] the effect of irradiation on λ_a for irradiation temperatures of 30 and 80 °C, using the Maxwell–Eucken model [Eqn.(4)] with the x values given in Fig.5 and λ_{cr} values from Ref.7. Increasing the dose to 5 Mrad produced a marked increase in λ_a (15%). Beyond this point λ_a increased more slowly (see Fig.9). The $\lambda_a = f(D)$ curve is identical in shape to $\lambda = f(D)$ for almost completely amorphous PE at T_m = 110 °C (see Fig.4).

Table 3. Effect of porosity on the thermal conductivity of amorphous polyethylene[24].

T_m, °C	$(1 - \lambda_{ae}/\lambda_a) \times 100$, %	
	D = 12 Mrad	D = 13 Mrad
20	6.0	16.0
40	5.8	13.0
60	5.3	11.4
80	4.1	9.8

The λ_a values for T_i = 80 °C could not be determined by this method because the samples of irradiated PE were found to be porous. It was argued[24] that for a given dose of radiation the ratio λ_a/ρ_a must be independent of the irradiation temperature, since the same mechanism was assumed to apply to both radiation-induced changes. The λ_a values obtained in this way were 2–4% higher than those for T_i = 30 °C: they correspond to the thermal conductivity which would be observed in samples without pores. By comparing these results with experimental data for λ_a (T_i = 80 °C) obtained at doses greater than ~ 10–12 Mrad (λ_{ae}), and therefore with almost fully amorphised PE, the influence of pores and cracks on λ_a was determined (see Table 3). The effect of porosity increases with dose of radiation and decreases with temperature.

It follows from those results[24] that an increase of T_m from 20 to 80 °C increases λ_a by 10%, which agrees with some published results[38,45,46] but not with others[7,9,37,39]. Evidently, in practice the dependence of λ_a on T_m is determined by the relative importance of two processes: the increase in free volume and the micro-Brownian motion of the sections of the polymer chain.

We have calculated the reliability of these results by allowing for the experimental error. Our analysis showed that if the measurement error of λ is ±4% the Maxwell–Eucken model

(like many other models) cannot give a reliable indication of the variation of λ_a with temperature, since the changes in this parameter between 20 and 80 °C are only 5–15% and lie within the uncertainty limits of the calculation. We must therefore conclude that the nature of the temperature dependence of λ_a in PE is still a live issue.

Nevertheless the gradual damping of the increase of λ_a produced by an increase in the absorbed dose[24] seems to support the micro-Brownian motion mechanism, since an increase in the number of radiation-induced cross-links should suppress this motion more rapidly than it lowers the molecular free volume.

2. Polytetrafluoro-ethylene

a) Density and crystallinity of polytetrafluoro-ethylene. Polytetrafluoro-ethylene (PTFE) is a partially crystalline polymer in which the degree of crystallinity (unlike that of PE) is increased by irradiation, even with small doses. This behaviour is explained by assuming the formation of molecular fragments (during the radiation-induced degradation) which can combine to form small crystallites[74,48]. Quantitative results on the increase in crystallinity caused by irradiation have been published by various workers[19,49–52]. The following dependence of the density ρ (kg m^{-3}) on the crystallinity x has been proposed[53]

$$\rho = 2000 + 300\,x \ .$$

Table 4. Density and crystallinity of polytetrafluoro-ethylene.

D, Mrad	ρ, kg m^{-3}	x, %	Refs.	D, Mrad	ρ, kg m^{-3}	x %	Refs.
0	2155	62	[19]	0	2156	—	[51]*
0.17	2234	72	[19]	0.001	2166	—	[51]*
1.26	2246	82	[19]	0.01	2183	—	[51]*
0	2154	54	[49]	0	2160	50	[52]**
0.05	2198	67	[49]	0.01	2210	65	[52]**
1.90	2222	74	[49]	0.04	2240	80	[52]**
0	2180	—	[51]	0	2190	60	[52]***
0.02	2221	—	[51]	0.01	2280	92	[52]***
1.00	2248	—	[51]	0.10	2290	95	[52]***

* Data for two samples with different initial densities.
** Irradiated *in vacuo*.
*** Irradiated in air. Density measured by i.r. spectroscopy.

Data on the effect of irradiation with γ quanta from ^{60}Co on the density and crystallinity of PTFE (for $T_m \cong 20$ °C) are given in Table 4. According to Ferse and co-workers[52] the volume of the pores produced in the samples by the irradiation was 0.57% for a dose of 10 krad and 1.4% for a dose of 40 krad. The melting point of PTFE decreases (as the dose of radiation is increased) from 340 °C for $D = 0$ to 334 °C for $D = 10$ krad and 314 °C for $D = 1$ Mrad[51]. This decrease in T_f is discussed by the authors in terms of an increase in the density of radiation-induced cross-links.

b) Thermal conductivity of polytetrafluoro-ethylene. Radiation-induced change in λ for PTFE have been observed[19,49]. It was found[49] that λ is practically independent of T_m between 10 and 180 °C, with a value close to 0.27 W m^{-1} K^{-1}. Small changes in λ were observed at $T_1 = 20$ °C and $T_2 = 125$ °C, and ascribed to a phase transition of the first kind in the crystal lattice of PTFE (T_1) and to relaxation processes in the amorphous phase (T_2). Irradiation with γ quanta from ^{60}Co to a dose of 1.9 Mrad (dose rate ~ 24 rad s^{-1}) gave a decrease in λ by 8%. At the same time T_1 fell by 1 K for $D = 0.05$ Mrad and by 14 K for $D = 1.9$ Mrad, while T_2 increased.

The changes in λ in PTFE can be explained by the two-phase model of a polymer. The λ value for the crystalline phase increases with temperature[7], since in complex crystals (like those of PTFE) the mean free path of phonons L is comparable to the mean free path for the amorphous phase. This can explain[7] the similarity between the temperature dependences of λ_{cr} and of λ_a. The relationship between λ_{cr} and λ_a for PTFE has been expressed in terms of the corresponding densities[54] as

$$d\lambda/\lambda = 5{,}8\ d\rho/\rho \ .$$

Since $\lambda_{cr} > \lambda_a$, the λ values for PTFE should increase with the degree of crystallinity, as has indeed been reported[53]. A decrease in λ on irradiation, accompanied by an increase in crystallinity, has been ascribed to porosity effects[49].

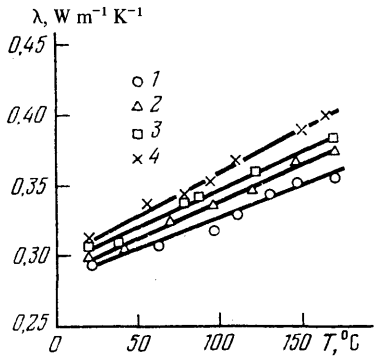


Figure 10. Temperature dependence of the thermal conductivity of polytetrafluoro-ethylene for different doses (D, Mrad): 1) 0, 2) 0.04, 3) 0.17, 4) 1.26[19].

A 6–12% increase in λ, depending on the measurement temperature, has also been observed[19] (as expected) in PTFE irradiated with γ quanta from ^{60}Co to a dose of 1.26 Mrad at a dose rate of ~ 8 rad s^{-1}. At the same time, and in contrast to earlier work[49], a monotonic increase of λ by 20–25% in the temperature range 20–170 °C was observed[19] in both non-irradiated and irradiated samples (Fig. 10).

The problem of the temperature dependence of λ in polytetrafluoro-ethylene is not yet fully resolved. Some workers[45,49,55,56] found λ to be practically independent of temperature, whereas others[19,57,58] noted an increase of λ with temperature above 0 °C. Irradiation produces an increase in λ.

3. Polypropylene

Tomlinson and Kline[59] have reported the effect of γ radiation (^{60}Co) on the density and specific heat of isotactic polypropylene (PP) at temperatures between 0 and 160 °C, doses up to 18 Mrad, and a dose rate of 26 rad s^{-1}. The initial crystallinity of the samples (x_0) was 60%.

The λ value of non-irradiated PP samples increases from 0.188 W m^{-1} K^{-1} at 0 °C to 0.200 W m^{-1} K^{-1} at 80 °C before decreasing monotonically to 0.130 W m^{-1} K^{-1} at 160 °C (Fig.11). Melting occurs in the range 127–167 °C; the melting peak corresponds to a temperature of 161 °C.

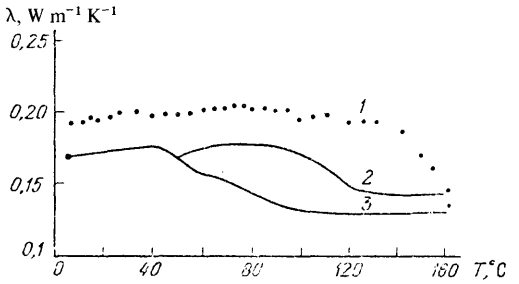


Figure 11. Temperature dependence of the thermal conductivity of polypropylene for different doses (D, Mrad): 1) 0, 2) 6, 3) 18[59].

Irradiation of PP causes breakdown of the crystals. The crystallinity is determined from the area under the exothermic melting peaks as x = 44% for D = 6 Mrad and x = 9% for D = 18 Mrad. Repeated heating does not affect the x value for D = 0, but it lowers the crystallinity from 44 to 14% for D = 6 Mrad and from 9% to 0 for D = 18 Mrad. These changes in crystallinity suggest a decrease in the size of the crystallites with increase in the dose of radiation, and this hypothesis is confirmed by the shift of the melting peak from 161 to 105 °C for D = 6 Mrad and to 63 °C for D = 18 Mrad. The density of PP at 20 °C decreases from 907 for D = 0 to 889 kg m^{-3} for D = 18 Mrad.

As in polyethylene, the λ value of PP decreases with dose of radiation. The maximum change in λ is 30%, and occurs at ~ 100 °C. At temperatures above T_m = 120 °C the thermal conductivity of irradiated samples becomes practically independent of temperature.

III. AMORPHOUS POLYMERS

The extent of radiation-induced changes in the thermophysical characteristics of amorphous polymers is determined mainly by the relative rates of radiation-induced cross-linking and degradation processes respectively. In polymers with a low radiation yield of cross-links, like polystyrene, we cannot expect marked changes in thermal properties. Polymers which suffer degradation under the influence of radiation, like poly(methyl methacrylate), will show changes in these properties: for example, a decrease in thermal conductivity.

1. Polystyrene

a) Specific heat of polystyrene. The specific heat of polystyrene (PS) at helium temperatures has been studied[60] with 2–16 Mrad doses of radiation consisting of 80 MeV electrons. In the calculation of the radiation-induced changes by the continuum model the effect expected from the deformation of the acoustic phonon spectrum was less than 0.5%: the effect actually found amounted to 25%.

The following is a possible mechanism for the change in c_p under the influence of irradiation. An important contribution to the low-temperature specific heat of amorphous polymers comes from low-frequency constrained vibrations of chain segments in regions of the sample where the density is less than the average value. The contribution from these vibrations may be decreased by radiation-induced cross-linking either through a decrease in the number of the segments or through an increase in their average vibration frequency. The radiation effect calculated by adopting this mechanism was 35%, i.e. fairly close to the experimental value.

We have studied[5] the effect of radiation on the specific heat of atactic PS at 30–200 °C with doses of up to 50 Mrad of mixed gamma and neutron radiation at a dose rate of 36 rad s^{-1}. At least up to 80 °C the specific heat of PS was found to be independent of the absorbed dose. The dispersion of the specific heat values for a confidence level of 95% was 0.7% at 30 °C and 1.8% at 80 °C. This result is not unexpected in view of the small distortion of the acoustic phonon spectrum.

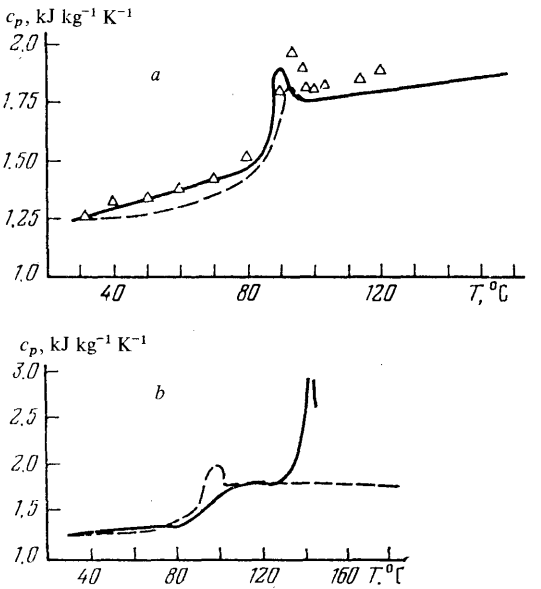


Figure 12. Temperature dependence of the specific heat of polystyrene: (*a*) D = 0, full curve first and second heating, broken curve third heating[5], experimental points from Ref.61; (*b*) D = 2.5 Mrad, full curve first heating, broken curve second heating[5].

Large radiation effects were obtained in the region of the thermal phase changes. Non-irradiated PS shows a sharp rise in c_p from 1.48 to 1.90 J g^{-1} K^{-1} at the glass transition temperature T_g = 87 °C (the average temperature of the glass formation region). These results[5] are fully consistent with earlier reports[61] (see Fig.12*a*). Other reports[62,63] of relaxation transition in the region of 50 °C were not confirmed[5,61].

Irradiation with a dose of 2.5 Mrad (Fig.12*b*) converts the maximum of c_p into a sharp break in the $c_p = f(T)$ curve, and increases T_g from 87 to 93 °C. Further irradiation produces a further increase in T_g (see Table 5).

Clearly defined high-temperature transitions, similar to the endothermic melting peak, were found[5] in samples irradiated with doses greater than 2.5 Mrad. The temperature (T_t) of these effects increased with dose (Table 5). In repeated heating runs the high-temperature effects had disappeared, and they could not be restored by any form of heat treatment.

Table 5. Temperatures of phase transitions in polystyrene[5].

D, Mrad	0	2.5	4.4	10	21	27	50
T_g, °C	87	93	90	97	94	97	102
T_t, °C	—	142	144	146	174	178	192

The presence of this transition in atactic non-irradiated PS was demonstrated[64] by various physicochemical methods including dilatometry, calorimetry, and X-ray diffraction. The transition temperature T_t lies between 115 and 225 °C, depending on the molecular weight of the PS. The appearance of the transition depends also on the heating rate. At low heating rates the transition may be shifted towards T_g, and overlap the glass formation process. In some samples of PS[5,61,65] this transition was not detectable for $D = 0$ because of the low heating rate used (≤ 1 K min^{-1}).

Boyer has pointed out[64] that T_t corresponds to the transition from one amorphous state (characterised by constrained rotations, due to interactions with neighbouring polymer chains) to another amorphous state (in which rotations are relatively free). This type of transition should be present in all amorphous polymers. At low molecular weights the two transitions (T_g and T_t) merge into one, and they can be resolved only if the molecular weight is of the order of 10^4. Unlike the glass formation process, which involves polymer segments of 50–100 carbon atoms, the high-temperature transition relies on the displacement of a whole polymer chain, made possible by the increase in the free volume and in the mobility of the polymer chains produced by changes in the position of their centre of gravity. In support of this model Boyer quotes the fact that the transition is suppressed by cross-linking the polymer (for example, in natural rubber or in polybutadiene).

The observation[5] of the high-temperature transition in irradiated PS at low heating rates, and of the disappearance of this transition in duplicated heating runs, is incompatible to some extent with the Boyer model. We suggest the following possible explanations: 1) the breakdown of relatively dense ordered regions of the quasi-crystal type formed during irradiation, whose size (and melting point) increase with dose, causing the transition temperature to increase; 2) relaxation of the mechanical stresses produced by the irradiation and therefore increasing with dose; 3) evaporation of liquid radiolysis products or the sudden ejection of gaseous products, whose diffusion is hindered under normal conditions.

A surprising analogy is noted between the dependence[5] of T_g and T_t on the dose of radiation (Table 5) and their dependence on the molecular weight of the PS[66]. Fox and Flory have shown[66] that T_g and T_t increase monotonically with the molecular weight, reaching values of $T_g = 100$ °C and $T_t = 192$ °C for $M = 360000$. Thus the radiation-induced cross-linking of PS appears to be equivalent to an increase in molecular weight from the point of view of the mechanism of the high-temperature transitions.

b) Thermal conductivity and density of polystyrene. According to the Klemens theory[67] of the thermal conductivity of amorphous materials the coefficient λ at low temperatures in these materials is determined by longitudinal acoustic phonons, whose mean free path L is determined by scattering phenomena associated with the elastic disordering of the amorphous solid structure. At low temperatures the characteristic wave lengths of the emitted phonons (and therefore also the L values) are much greater than the size of the disordered regions. From this point of view the formation of transverse bonds in the PS as a result of radiation-induced cross-linking will only produce additional point defects in an already disordered structure, and it should not have a marked effect on λ, as long as the average distance between cross-linking points remains greater than the wave length of the phonons (~ 10 Å).

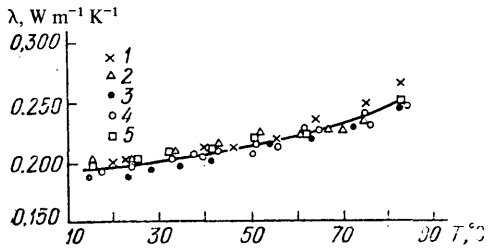


Figure 13. Temperature dependence of the thermal conductivity of polystyrene for different doses (D, Mrad): 1) 0, 2) 2.5, 3) 10, 4) 21, 5) 27[19].

Since the radiation yield of cross-links is small in PS, large changes in λ cannot be expected, even for large doses. Thus, no changes in λ could be detected (within experimental error) with doses of 2–16 Mrad at helium temperatures[60] and with a dose of 27 Mrad at 16–85 °C.[19] On the other hand, an increase in temperature from 16 to 85 °C increases the λ value of polystyrene by 24% (Fig.13). A small increase in the density of PS (by 0.6% at 20 °C) has been noted[19]: clearly, this cannot cause a large change in λ. The distortion of the spectrum of acoustic phonons caused by the transition from helium temperatures to the region of 50–100 °C is clearly insufficient to make the L value comparable with the distance between cross-linking points.

2. Poly(methyl methacrylate)

Poly(methyl methacrylate) (PMMA) is one of the polymers which are degraded by radiation. Therefore we can expect (from the above considerations) relatively small changes in λ for fairly high doses of radiation.

Knappe and Yamamoto[18] studied λ in PMMA by using samples cross-linked with triallyl cyanurate (TAC) or samples of PMMA irradiated to doses of 20 Mrad at a dose rate of 17 krad s^{-1}. For a 10% weight fraction of TAC the molecular weight of PMMA fell from 3.2×10^4 to 8.2×10^3 and the density rose from 1184 to 1191 kg m^{-3}, giving a maximum increase in λ of 10%.

Irradiation of the PMMA to a dose of 1 Mrad had no effect on λ. At a dose of 2 Mrad and T_i = 25 °C the λ value fell by 5–6%. The degradation of the polymer is shown by the decrease in molecular weight (22800 at a dose of 1 Mrad and 10700 at a dose of 2 Mrad). This decrease in molecular weight increases the number of end-groups of macromolecular chains, corresponding to an increase in the relative number of van der Waals bonds, i.e. to a decrease in λ.

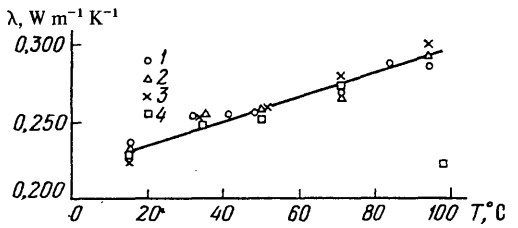


Figure 14. Temperature dependence of the thermal conductivity of poly(methyl methacrylate) for different doses (D, Mrad): 1) 0, 2) 0.1, 3) 0.3, 4) 0.6[19].

These results were confirmed by measurements in our laboratory[19], in which PMMA was irradiated with γ quanta from ^{60}Co to doses of 0.09 and 0.57 Mrad at a dose rate of 3.6 rad s^{-1}. The λ values measured at 18–98 °C increase with temperature by 25% and are independent of dose (Fig.14). At 98 °C a dose of 0.57 Mrad produces marked frothing which causes a sharp drop in λ.

IV. ANALYTICAL MODELS OF HEAT CONDUCTION MECHANISMS

In order to predict radiation effects on the thermophysical properties of polymers we need analytical models which adequately describe the observed changes in these properties.

In some early descriptions[68,69] of the thermal conductivity of amorphous materials the polymer was treated as a series network of elementary thermal resistances corresponding to chemical and to van der Waals types of bonding between atoms. The standard Debye formula for phonon heat conduction was used. According to the elastic constants of these bonds, the thermal conductivity along the main polymer chain is 10 times greater than between chains.

For a series network of thermal resistances equivalent to a cross-linked polymer with n carbon atoms in the chain between the cross-linking points the parameter λ_c can be expressed as

$$\frac{1}{\lambda_c} = \frac{1}{3}\left(1+\frac{r}{2}\right)\frac{1}{\lambda_1} + \frac{1}{3}\left(2-\frac{r}{2}\right)\frac{1}{\lambda_2} + \frac{1}{3n}\left(\frac{1}{\lambda_2}-\frac{1}{\lambda_1}\right),$$

where λ_1 and λ_2 are the coefficients for the thermal conduction along the chain and between chains respectively, and $r = (M_n/M_c - 1)/n$ is the cross-linking parameter. (M_n is the number-average molecular weight before cross-linking, and M_c is the molecular weight of the chain portions between cross-links.)

For a cross-linked polymer it seems more logical to postulate a series–parallel equivalent network of thermal resistances. If we assume that the radiation effects appear mainly in the cross-links between polymer chains we can confine the changes in thermal resistance to the direction perpendicular to the chains. Under these conditions we can write[18]

$$\lambda_c = 3\frac{\frac{r}{4}\lambda_1 + \left(1-\frac{r}{4}\right)\lambda_2}{\left(\frac{r}{4}+2\right)\lambda_1 + \left(1-\frac{r}{4}\right)\lambda_2}\lambda_1 . \qquad (5)$$

A comparison[18] of calculation and experiment for irradiated polyethylene above the melting point of the crystals and for poly(methyl methacrylate) chemically cross-linked with triallyl cyanurate showed that the λ_c values given by the formulae for series or parallel connection lie well below the experimental values. Calculation by formula (5) gives much better agreement with experiment, though the discrepancy increases with the degree of cross-linking.

One possible reason for the discrepancy is the use of too rough an approximation for the parameter r, by taking the limit

$$r = \lim_{n\to\infty}\left(\frac{M_n/M_c - 1}{n}\right) = \frac{M_g}{M_c},$$

where M_g is the molecular weight of a monomer unit in the chain. It could be useful to determine the absolute values of λ_1 and λ_2 from experimental data for both irradiated and non-irradiated polymers, and to use these values in tests of the various models of thermal conductivity.

V. ANISOTROPY OF THERMAL CONDUCTIVITY

It is clear from the above discussion that crystalline or partially crystalline polymers can show changes in thermal properties on irradiation as a result of changes in phase composition. For amorphous polymers, or for the amorphous phase of partially crystallised polymers, the radiation effect depends on the number of the resulting radiation-induced cross-links and on the extent of degradation of the material. When the yield of cross-links is quite high, for example in the amorphous phase of polyethylene, the radiation effects are substantial. When the yield of cross-links is low (for example, in polystyrene) radiation-induced changes in thermal conductivity are not detected, and in easily degraded materials (for example, poly(methyl methacrylate) and thermal conductivity decreases. At the same time chemical cross-linking of the polymer chains causes λ to increase.

It is interesting to compare the effect of transverse links between the polymer molecules on the λ value of the polymer with anisotropy effects in the thermal conductivity of polymers. The basic reason for anisotropy in the thermal properties of polymers is the difference between the transport of heat along the macromolecular chains and the transport between the chains. Thermal vibrations in the macromolecule are transmitted much more rapidly along the main covalent bonds than along the side bonds. Intermolecular heat transfer in an amorphous polymer is characterised by a definite potential barrier (or thermal resistance) which opposes the transfer of thermal impulse created by the van der Waals interaction forces.

Experimental data (for polystyrene, poly(methyl methacrylate), poly(vinyl chloride), and polycarbonate) on the stretch (η) of oriented polymers gave the following relationship between λ and the thermal expansion coefficient β[2]:

$$\frac{\lambda_\eta}{\lambda_0} = 0.8\frac{\beta_\eta}{\beta_0} + 0.2,$$

where the subscript "η" denotes a stretched polymer. As η is increased, both λ and β increase linearly in the stretch direction, and in the transverse direction both parameters

decrease. The smallest anisotropy is found in polystyrene, and the largest in polycarbonate. The longer (or bulkier) the side-groups in the main chain, the less marked is the anisotropy.

By interpreting the cross-linking of polymer chains as an increase in size of the side-groups in the macromolecule we can establish an analogy between the radiation-induced cross-linking and the mechanical deformation of a polymer, i.e. we can compare the absence of radiation effects on the λ value of an amorphous polymer with the absence of anisotropy in its properties. Conversely, strong radiation effects on λ suggest that anisotropy can be expected. Thus, the anisotropy of λ and β is found[2] to be much more marked in PMMA than in PS. Similar effects from cross-linking (radiation-induced in PS[19,60] and chemical in PMMA[18]) have been obtained for the thermal conductivity of these materials.

If our hypothesis is valid it offers a practically useful corollary: dilatometric measurements of the linear expansion coefficient of non-irradiated polymers could be a valuable tool in studies of radiation effects in the thermal conductivity of polymeric amorphous materials. Clearly, in the absence of substantial anisotropy in the β values the need for radiation experiments disappears.

VI. COMPOSITE MATERIALS

Whereas the polymers considered above are to some extent model materials, for which an analysis of the radiation effects can be fairly reliable, in the case of the practically very important composite materials a comparable analysis is often impossible in our present knowledge of the mechanism of physicochemical phenomena in polymers. The main difficulties arise from the structural complexity of the polymers, from the frequent lack of information on the properties of the separate components, from the non-additivity of those properties, etc.

Dosimetry can present a very difficult problem in composite systems. If the particle size of the components is of the order of a tenth of a millimetre or less in a system where electronic equilibrium is not reached, irradiation with γ quanta or with fast electrons[70] leads to a substantial redistribution of the absorbed energy between substances with different effective atomic number Z, while retaining the overall balance: the dose absorbed by the substance with the smaller value of Z increases, and the dose absorbed by the substance with the larger value of Z decreases. As a result the conventional calculation of average radiation dose can be seriously misleading, since some components of the composite are almost invariably "over-irradiated" while others are "under-irradiated". The magnitude of this effect can reach several tens of per cent, and in some cases 100%, depending on the type (and spectrum) of the radiation.

Evidently, the only prospect of a realistic prediction of radiation-induced changes in the thermophysical properties of composite materials lies in an extensive study of model substances, in the characterisation of the radiation-induced changes in these substances, and in the development of a unified theory of radiation effects on thermophysical properties, followed by application of the results to composite materials and detailed experimental tests of theoretical predictions.

Published experimental data on radiation effects in the thermophysical properties of these materials relate to the thermal conductivity of the composites VK-9 and Kriosil[71]. The VK-9 resin is a compound of the epoxide oligomer ED-20 and polyamide PO-300, and Kriosil consists of the organosilicon polymer DFMKr, the low-molecular polyamide L-20, boron nitride, and Aerosil. Irradiation was carried out with γ quanta from ^{60}Co at 30 °C in air, or in a reactor at 50 °C. The results of our study of VK-9 are summarised in Table 6, those for Kriosil in Table 7.

The radiation-induced changes in these composites were analysed by the two-phase model for partially crystalline polymers, using Eqn.(4). In order to establish whether the decrease in the thermal conductivity of VK-9 on irradiation is due to amorphisation of the partially crystalline polyamide or to degradation of one or both polymers we calculated the λ and λ_a/λ values of the polyamide from published data[72].

Table 6. Thermal conductivity of VK-9, W m^{-1} K^{-1}.[71]

D, Mrad	−100° C	0° C	100° C	180° C
0	0.210	0.231	0.260	0.289
1	0.202	0.224	0.251	0.282
3	0.197	0.219	0.248	0.276
10	0.188	0.219	0.245	0.269
20	0.151	0.186	0.224	0.248

Table 7. Thermal conductivity of Kriosil, W m^{-1} K^{-1}.[71]

D, Mrad	−100° C	0° C	100° C	180° C
0	0.570	0.728	0.810	0.859
1	0.514	0.686	0.748	0.796
2.2	0.500	0.656	0.720	0.756
6.6	0.479	0.600	0.665	0.693
10	0.431	0.576	0.632	0.659
20	0.369	0.479	0.528	0.583

The experimentally observed change in λ for VK-9 at a dose of 20 Mrad is 1.3–2.3 times greater than the change corresponding to full amorphisation of the polyamide (allowing for its proportion by weight in the compound). An analysis of the density of different polyamides as a function of crystallinity, and a study of the changes in density of VK-9 as a function of dose, showed that the amorphisation of the polyamide is far from complete even at a dose of 20 Mrad. It follows that the degradation of the VK-9 resin under the influence of radiation makes a significant contribution to the observed changes in λ. However, further work is needed to determine whether both polymers are degraded or only one, and to what extent.

At temperatures near −50 °C the $\lambda = f(T)$ curves show maxima which gradually decrease as the dose is increased. These maxima disappear at a dose of 20 Mrad. They appear to be related to the glass transition in the components of the polymer. This suppression of a phase transition of the second kind has been observed previously, for example in the specific heat of irradiated polystyrene[5]. A possible explanation is the formation of micro-inhomogeneities during irradiation, each new structure having its own glass transition temperature. The result is a "smearing out" of the phase transition in temperature.

The amorphous polymers (organosilicon polymer and polyamide) in Kriosil are typical of the polymers which are degraded by irradiation. We know[73] that in filled polymers the rate of radiation-induced degradation is much higher than in unfilled organosilicon vulcanised materials, possibly as a result of the stress concentration on the chains in contact with the filler particles. It is clear from the decrease of the

λ value of Kriosil with increase in the dose of radiation (Table 7) that in this system the cross-linking processes cannot compete with the degradation processes. The monotonic decrease in density of Kriosil with dose of radiation (by 12%) is also consistent with the degradation hypothesis.

We note that whereas in Kriosil the magnitude of the radiation effects is almost independent of the temperature at which λ is measured, in the case of VK-9 the change in λ at -100 °C is almost double that at +100 °C. This may be due to the large difference between λ_{cr} and λ_a for the polyamide ($\lambda_{cr}/\lambda_a = 2.0$ at -100 °C and 1.68 at +50 °C), or to a difference in their temperature dependence. Whereas the relationship obtained by Eucken[25] for low-molecular crystals ($\lambda_{cr} \propto 1/T$) applies in our case, the parameter λ_a increases with temperature up to the glass transition point and then slowly decreases.

In both composites the radiation effects were unaffected by the type of radiation used.

VII. REVERSIBLE EFFECTS ON THE THERMOPHYSICAL PROPERTIES

Reversible effects include changes in the properties of polymers initiated by irradiation but which disappear as soon as the irradiation is stopped. These effects can be very strong in the dielectric (and in some of the mechanical) properties of polymers, but as far as the writer is aware no such observations have been reported for the thermophysical properties. This may be due, at least in part, to the practical difficulty of this type of work.

Indirect evidence for the absence of reversible effects in the thermal conductivity of polyethylene comes from our relaxometer[70] study of the components of the absorption from nuclear reactors. The detector of the relaxometer was a rectangular polyethylene prism 50 × 50 mm in cross-section and 150 mm long. From the thermal conductivity coefficients of polyethylene measured after irradiation the temperature fields in the cross-section of the prism were calculated: the results agreed well with those of irradiation experiments at 50–100 °C with doses of up to 10 Mrad and dose rates between 13 and 55 rad s^{-1}.

Radiation-induced gas evolution is a possible reason for the appearance of reversible effects in the specific heat of polymers. At high enough dose rates the pressure of gaseous radiolysis products (mainly hydrocarbons) in the microvolumes of irradiated samples can reach several MPa. On reaching a particular pressure, depending on the mechanical strength of the polymer, the irradiation temperature, etc., the sample develops microscopic cracks and pores. This process continues as long as the absorbed dose continues to increase. The polytropic emission of radiolysis gases involves a decrease in temperature according to the laws of thermodynamics, and therefore it should lead to a change in the "apparent" specific heat of the material. This mechanism may be more easily observed for irradiation temperatures below 0 °C, when the polymers are less plastic.

No reversible effects were noted within experimental error (±5%) in our recent measurements of the specific heat of polyethylene and Kriosil irradiated at 20–90 °C and dose rates of 5.5–11 rad s^{-1} to a dose of 2 Mrad. According to our model these effects (if they exist) can be expected only for doses and dose rates an order of magnitude higher than those used in these experiments†.

† Essentially reversible effects were observed in very recent experiments on the specific heat of polyvinylformal (see B.A.Briskman. et al., Vysokomol.Soed., in press).

VIII. STORED ENERGY OF IONISING RADIATIONS

The analytical prediction of the effect of radiation on the properties of polymers, including their thermophysical properties, requires a knowledge of the energy balance of the interaction between the ionising radiation and the substance.

During the interaction of γ quanta, electrons, or neutrons with the substance being irradiated most of the energy of the secondary electrons or charged heavy particles is dissipated through intermediate forms of excited or ionised atoms and molecules. In the majority of materials the ionisation energy is rapidly converted into heat by recombination processes. However, some of the energy absorbed during irradiation is not converted into heat: this is usually called the stored energy ΔW. Storage can occur, for example, by the formation of crystal defects. In polymers a very important form of energy storage is the generation of cross-links between polymer chains.

Most of the published experimental data on ΔW are estimates of the upper limit of this parameter, obtained from dosimetric measurements directly within the material. The following is a list of the relative values of ΔW for polyethylene (as a percentage of the total energy absorption) obtained in different laboratories: ΔW (%) = 3,[74] 2,[75] 3.7,[76] 0.7,[77] 4,[78] and 3.8%[79].

Weimer[78] found that in polyethylene and for doses up to 1 krad the predominant reaction is exothermic, with a maximum heat evolution at the beginning of the irradiation which accounts for more than 20% of the energy in the absorbed dose. At doses in the region of 1 krad the exothermic reaction is replaced by an endothermic reaction (with energy storage); at a dose of 2 krad the parameter ΔW reaches 4%, and stays constant at higher doses. Polystyrene also shows a characteristic exothermic reaction[78], but when the dose exceed 2 krad, $\Delta W = 0$. In a plastic equivalent to biological tissue with effective atomic number Z proton irradiation gave[76] $\Delta W = 4.2 \pm 0.3\%$. Sabel and co-workers[79] used X-radiation of 30 keV energy and obtained the following values of ΔW: 2.31 ± 0.78% for poly(methyl methacrylate), 6.95 ± 0.94% for polyamide, 2.01 ± 0.68% for poly(vinyl chloride), and 4.08 ± 0.55% for Shonka-plastic. The exothermic effect reported[78] for PE was not observed in this work[79], but it was observed for PMMA.

Differences in stored energy for different types of radiation have not been reported. Though the selectivity of the interaction of different types of radiation with the thermophysical properties of polymers has not been specifically examined, we have no reason to expect any marked differences, especially at temperatures above 0 °C.

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From this analysis of the work published so far we may conclude that further studies of the thermophysical properties of irradiated polymers should be aimed at the following problems: 1) the creation of a basic theory of the effects of radiation on the thermophysical properties; 2) the study of likely reversible effects in these properties; 3) the study of the selectivity of interactions with different types of radiation; 4) the extension of the range of model polymers and of the range of characteristics for which detailed information is available. In particular, we need data on the behaviour of the linear thermal expansion coefficients.

The solution of these problems should allow the prediction of the after-effects of radiation on the thermophysical properties of polymers, including composite materials, which is currently of interest in both pure and applied science.

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Chemical X-Ray Fluorescence Trace Analysis

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The results of recently published work on the determination of traces of elements by X-ray fluorescence (XRF), combined with chemical methods of separation and concentration, have been reviewed. The application of various combinations of XRF with precipitation, sorption, and extraction has been described. The combined XRF method can be used to determine traces of elements in natural and industrial materials.
The bibliography contains 84 references.

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I. INTRODUCTION

In the determination of traces of elements by X-ray fluorescence (XRF), there are several ways of increasing the sensitivity. One is by improving the quality of the apparatus and by using new and more sensitive X-ray spectrometers. This method is not always possible, however, and often does not give the desired results. Thus in a large number of recent studies, the sensitivity of XRF analysis has been increased by preliminary physicochemical and chemical concentration of the elements being determined. Concentration combined with XRF is also convenient in that specimens of uniform composition and form are obtained; this eliminates the complex calculations required to take account of matrix effects.

The following methods are used for concentration in chemical analysis: extraction, sorption, precipitation, evaporation, electrochemical methods, crystallisation processes, zone fusion, and various others[1]. Only those methods of concentration giving specimens convenient for XRF spectrometry are combined with XRF, however.

II. COMBINATION OF X-RAY FLUORESCENCE ANALYSIS WITH PRECIPITATION

The combination of precipitation with XRF determination gives good results, since preliminary separation and selective precipitation make it possible to separate traces of elements from a matrix and also from elements giving interfering spectral lines. On the other hand, the precipitated elements are uniformly distributed in the light matrix of the emitter on a comparatively large surface, increasing the accuracy and sensitivity of the determination.

In an examination of the results of studies based on the combination of precipitation with XRF, mention must first be made of a paper published in 1963 by Luke[21], who showed that this combined method makes it possible to determine traces of 69 elements in organic and inorganic materials, and examined in detail the problems associated with the precipitation, coprecipitation, and filtration of the precipitates, the influence of interfering ions, the use of different precipitants (carbamate, Cupferron, NH_3, H_2S, phenylfluorone); the conditions for the chemical separation of 25 elements and their X-ray analysis were also examined. Luke showed that the method is fairly rapid and sensitive, and makes it possible to determine 2×10^{-8} g Ni, Ti, and Sc; 10^{-7} g Ca, Cu, Fe, Co, and Zn; and 10^{-6} g of a number of other elements.

Another fundamental paper in this field was published by Hirokawa[3], who clearly showed that the combination of XRF with concentration by precipitation is effective and has a high sensitivity. Other studies in this field can be formally divided into two groups, involving the use of inorganic or organic compounds.

1. The Use of Inorganic Precipitants

Traces of elements are usually precipitated as the sulphides, sulphates, or hydroxides. Precipitates of inorganic salts and hydroxides are readily analysed by XRF. It should be borne in mind, however, that possible agglomeration of the precipitate may lead to distortion of the surface of the emitter, with an undesirable effect on the results of the analysis. To prevent this phenomenon, it is recommended that sulphide precipitates be filtered immediately after precipitation. The precipitation of inorganic compounds is widely used for the XRF determination of traces of many elements.

Thus, in the analysis of metallic aluminium for traces of Cu, Fe, Mn, Zn, and Co, the precipitation of these elements as the sulphides made it possible to determine their concentrations at the 10^{-4}% level[4].

An interesting method for determining Hg, Ag, Cu, Bi, Pb, Cd, Se, Te, Zn, Co, and Ni in aqueous solutions is based on the filtration of the solution through a thin layer of zinc and manganese sulphides; the metals listed form less soluble sulphides, and remain in the precipitate, which is then analysed by XRF.[5] In addition to traditional methods of precipitating metals as the sulphides, their determination in precipitates of hydroxides[6-8], oxides[9], and sulphates[10] is also used. The detection limit of elements such as Pb, Nb, Ta, and W in steels and alloys is ~0.002%.[6,10]

The XRF analysis of the precipitates obtained is carried out using an external standard, and the reference specimens are prepared as the same precipitates. In addition to external standards, internal standards can also be used. Thus in the determination of U, Np, Pu, and Am,[7] the internal standards added to the solution are Y and Sc, which are then precipitated together with the other elements using NH_4OH.

Uranium has been determined[11] at the 10^{-4}% level after precipitating as barium diuranate; the precipitate was sorbed not on the polycarbonate membrane usually employed, but on an Ag membrane filter. This lowered considerably the minimum quantity of uranium detectable, as a result of the excitation of the fluorescent emission of uranium not only by the primary radiation of the X-ray tube but also by the secondary emission from the silver support.

Precipitation is being used successfully to determine not only heavy metals but also various light elements. Thus phosphorus can be determined in purified copper at the level of 5×10^{-4}% in a 5 g specimen with preliminary precipitation of phosphorus by ammonium molybdate[8]. The quantity of phosphorus can be determined from the fluorescent emission of phosphorus and molybdenum. The determination of parts per million of chlorides in various silver catalyst specimens has been described[12]. Good results can be achieved by coprecipitating traces of elements with iron[13,14] and cobalt[15] hydroxides; the method described above is used to prepare the emitters.

2. The Use of Organic Precipitants

Most of the work based on a combination of precipitation with the XRF determination of elements has been carried out using organic precipitants[16]. Mention must first be made of those studies where heavy metals have been precipitated using sodium and ammonium carbamates.

Thus sodium diethyldithiocarbamate has been used to determine traces of Cu, Zn, Hg, and Fe in salt solutions[17,18] and of Cu, Zn, Cd, and Pb in aqueous solutions[8], to determine the principal components of Mn,Zn- and Ni,Zn,Co-ferrites[19], in the multi-element analysis of sedimentary and other rocks[20], and to determine low concentrations of Mn and Fe in titanium[21]. Kessler and co-workers[22,23] used titanium diethyldithiocarbamate to coprecipitate traces of transition metals. Japanese workers have determined traces of Cu, Zn, Fe, and Ni in pure aluminium and magnesium by precipitating with ammonium pyrrolidine-1-dithiocarbamate; the XRF analysis of the precipitate was carried out using an external standard. For this purpose, selenium was added as internal standard to the solution[24]. The concentrations of Fe, Co, Cu, Zn, Cd, and Pb in water at the 10^{-9}% level were determined by coprecipitating these metals with Mo pyrrolidinethiocarbamate complex carrier[25]. Cr, Cu, Zn, As, and Se in water at the 10^{-7}% level was determined similarly, except that the carrier used to coprecipitate these elements was the Fe pyrrolidinedithiocarbamate complex[26].

Methods have also been described for determining heavy metals by coprecipitating with polyvinylpyrrolidone and thionalide[27], by precipitating as salts of glycollic acid[28], and by coprecipitating Co and Ni with iron hydroxide using hexamethylenetetramine[29].

Traces of tungsten in iron, molybdenum, and titanium have been determined by precipitating the tungsten with phenylfluorone solution after dissolving the metal specimen[30]. A method has also been proposed for the simultaneous XRF determination of Nb, Zn, and Ta at the 10^{-2}% level after precipitating with phenylarsonic acid[31]. It has been shown possible to determine transition metals after precipitating them with 1-(2-pyridylazo)-2-naphthol[32]. Standard XRF methods for determining Fe at the 10^{-4}% level include its determination after precipitating with 1-(2-pyridylazo)-2-naphthol[33].

In the determination of traces of Al, Fe, and Ti in different gypsum specimens, the metals were precipitated by Cupferron from acidic solutions (pH 3.5–3.7) after dissolving the gypsum by fusing with H_3BO_3 and Na_2CO_3 followed by solution in H_2SO_4.[82] This method gives good reproducibility, the coefficient of variation does not exceed 2.6%, and the minimum detectable quantities of Al, Fe, and Ti are 0.15, 0.58, and 0.15 μg respectively.

Sometimes, not one but several precipitants are used to precipitate micro-quantities of metals. In those cases where both precipitants are organic reagents, however, multiple precipitation may not take place, since the first precipitant forms complexes and prevents the precipitation of some elements by the second precipitant. This effect can be observed when Cupferron and phenylfluorone are used in succession. On the other hand, a successful combination of reagents gives good results.

Thus traces of Mn, Fe, Ni, Cu, Zn, Cd, Sm, Hg, and Pb have been coprecipitated from solutions using a mixture of 1,10-phenanthroline and sodium tetraphenylborate in the ratio 1:1.[34] Tetraphenylborate is also used to precipitate K and Rb.[20,35] In all the procedures described, the precipitates were filtered through microporous membranes or compact filters, and the specimens obtained in this way were studied by XRF spectrometry. A special apparatus has been developed for the selective electrodeposition of Ni, Cu, and Zn, and the XRF analysis of the deposit[36].

Thus the combination of precipitation and XRF determination is rapid, sensitive, accurate, and, which is most important, universal. It is necessary, however, to remember the possible errors, associated with incomplete precipitation of the elements to be determined or the coprecipitation of elements which interfere with one another in the XRF determination, and also the marked difference between the actual and theoretical density of the precipitate. Examples of the combination of XRF with precipitation are given in Table 1.

Table 1. Examples of combined XRF analysis and precipitation.

No.	Precipitant	Material	Elements determined	Refs.
1	Sodium diethyldithiocarbamate	salt solutions	Cu, Zn, Hg, Fe^{3+} (0,01—10 mg litre^{-1})	[17, 18]
2	ditto	water, pH 5.5	Cu, Zn, Cd, Pd	[8]
3	»	ferrites	Mn, Zn, Ni, Co, Fe (~ 5 μg)	[19]
4	»	water, pH 8.0–8.2	transition metals	[22, 23]
5	»	titanium, pH 7–9	Mn, Fe (50–100 μg)	[21]
6	»	ores and sedimentary rocks	Ti, Mn, Fe, Ni, Cu Zn, Pb, As, Sr	[20]
7	Ammonium molybdate	purified copper	P ($3 \cdot 10^{-4}$%)	[8]
8	$La(NO_3)_3 + NH_4OH$	crude copper	As, Bi, Fe, Pb, Sb, Te, Sn	[8]
9	*	solutions	Ni, Cu, Zn ($1 \cdot 10^{-100}$%)	[36]
10	Sodium tetraphenylborate	water	K (0.1–1000 μg)	[35]
11	1,10-Phenanthroline + Na tetraphenylborate (1:1)	water, pH 4–6	Mn, Fe, Ni, Cu, Zn, Cd, Sn, Hg, Pb, Co	[34]
12	1-(2-Pyridylazo)-2-naphthol	water, pH 10	Cu, Zn, Fe, Co, Ni (0,1—0.5 μg in 50 ml)	[32]
13	Pyridylazonaphthol	molybdenum, pH 10	Fe ($5{,}6 \cdot 10^{-4}$—$5 \cdot 10^{-3}$%)	[33]
14	Phenylarsonic acid	steel	Nb, Zr (0,01%)	[31]
15	Phenylfluorone	iron, 1% H_2SO_4 solution		[30]
16	Glycollic acid	organic material, water, pH 4.7–5.0	Hg, Ni, Pb, Se, As, Cd, Cu, Fe, Zn ($5 \cdot 10^{-6}$—$2{,}5 \cdot 10^{-5}$%)	[28]
17	Polyvinylpyrrolidone-thionalide	water, pH 4	Sn, Te, Hg, Pb (30—600 μg litre^{-1})	[27]
18	Ammonium pyrrolidinedithiocarbamate	water, pH 4	Cr, Cu, Zn, As, Se (10^{-7}%)	[26]
19	ditto	water	Fe, Co, Cu, Zn, Pb (10^{-9}%)	[25]
20	»	water	Cu, Zn, Fe, Ni, Mg, Al (< 50 μg)	[24]
21	NH_4OH	RuO_2	Th (0,1—1,2%)	[9]
22	ditto	water	U, Np, Pu, Am (0.05 μg)	[7]
23	»	Cu (metal), pH 9–10, Fe^{3+} ions	Bi	[14]
24	»	pH 8.5, Fe^{3+} ions	Zn, Cu, Pb, Mn (10—75 μg)	[13]
25	Na_2S	aluminium	Fe, Mn, Zn, Cu (10^{-4}%)	[4]
26	ZnS+MnS	water	Hg, Ag, Cu, Bi, Pb, Cd, Sn, As, Se, Tl, Zn, Co, Ni	[5]
27	H_2SO_4	steel, Ba^{2+} ions	Pb (0,02—0,5%)	[10]
28	H_2SO_3	Fe alloys	Nb, Ta, W ($2 \cdot 10^{-3}$%)	[6]
29	NaOH	molybdenum	Zr, Ti (10^{-8}—10^{-7} r)	[15]
30	Cupferron	gypsum, pH 3.5–3.7	Fe, Al, Ti	[82]
31	8-Quinolinol	water, activated carbon	heavy metals	[38]
32	8-Quinolinol	water, pH 8, activated carbon	ditto	[39]

*Electrodeposition.

III. X-RAY FLUORESCENCE ANALYSIS COMBINED WITH ION EXCHANGE AND SORPTION

In 1977, Leyden[37] reviewed XRF methods for determining metal ions in water specimens with preliminary concentration[37]. The most promising methods of concentration were sorption methods, particularly those using special filters and membranes with immobilised ionogenic groups. All the work reviewed[37] can be divided into two groups. The first involved the sorption of the metals or their complexes on activated carbon, or ion-exchange concentration on a resin. The concentrates obtained were generally subjected to further treatment to obtain an emitter convenient for XRF. The second group involved the use of ion-exchange membranes and paper, and in this case the concentrate was obtained in a form suitable for the XRF determination of the elements.

1. The Use of Ion Exchange Resins and Activated Carbon

The sorption of metal chelates on activated carbon is well known. This property has been used by a number of workers to concentrate heavy metal oxinates on activated carbon with subsequent XRF determination of the metals in the concentrate[38–40,80]. The authors cited not only developed a quantitative method for determining Mn, Fe, Co, Ni, Cu, Zn, and Al in waters of different types but also found the quantitative characteristics of the dependence of the distribution of the complexes of these elements with 8-quinolinol on various factors (pH, reagent concentration, metal concentration, etc., and also the presence of large quantities of alkali and alkaline earth metal ions in the solution).

Transition metals are often concentrated using the commercially available ion exchanger Chelex-100 (a complexing ion-exchange resin of the ketoimine–carboxylate type). This resin has been used to determine uranium in ground water[41]. A weighed specimen of the resin was placed in a previously acidified solution of the water being analysed, after which the resin with the sorbed uranium was filtered off on a membrane filter, dried, and compressed with a binding agent (Somarmix) on a boric acid support. The disc obtained in this way was used for the XRF analysis; the uranium detection limit was 2×10^{-7}%. Ca^{2+}, Ti^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, As^{3+}, and Br^- were determined similarly in solutions containing these elements at concentrations of 5×10^{-6} to 5×10^{-4}%.[42]

In some cases, however, a dynamic method of ion-exchange concentration is more convenient. For example, Cu and Ni have been determined at the 0.5–5 μg litre^{-1} level, and Zn at the 4–15 μg litre^{-1} level in sea water[43]. The sea water was passed through a column of resin, after which the resin with the sorbed ions was compressed to form a disc. The minimum detectable quantities of Cu, Ni, and Zn are 0.3, 0.1, and 0.1 μg litre^{-1} respectively. A similar method has been used[44] to determine traces of a number of elements in various materials.

An interesting method for determining lead and mercury[45] using diethyldithiocarbamate on a support of Chromosorb W-DMCS gives 100% concentration. The detection limits for cadmium and mercury are 0.08 μg and 1.7 μg respectively[45].

Several papers in this field have been published in the Soviet literature. An X-ray–radiometric method, combined with ion-exchange concentration, has been used to determine noble metals (gold, rhenium, and silver);[49] the detection limit was 0.1–0.01 mg litre^{-1}. In the determination of Cu, Zn, Cd, and Pb in sewage[81], the metals were concentrated using the strongly acidic monofunctional KU2×8 cation exchange resin.

Amberlite IRA-400 in the Cl form has been used to determine low concentrations of uranium [$(0.2–5) \times 10^{-4}$%] in carbonate–bicarbonate solutions. To prepare the emitter, the resin with the sorbed uranium was filtered off and distributed in a uniform layer on a Mylar film fixed in a special holder[48].

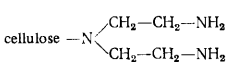
In the development of this trend in XRF, research workers are now using new and more selective sorbents. Japanese workers have developed a method for determining microgram quantities of metals by XRF combined with extraction from solutions by chelating functional groups immobilised on SiO_2.[47] A whole series of new sorbents have been prepared and studied in detail, together with the conditions for the extraction of Hg, Cu, Zn, Ni, Pb, Eu, and Mn as the preliminary concentration stage in XRF analysis[80]. A disadvantage of sorbents of this type is their instability in concentrated acids and alkalies.

Substituted cellulose powder containing 1-(2-hydroxyphenylazo)-2-naphthol or 4-(2-pyridylazo)resorcinol groups has also been proposed for concentrating metals in XRF analysis[45]. The combination of ion-exchange concentration on a column and XRF determination of the elements in the resin phase is not very convenient, however, since the preparation of a suitable emitter for XRF spectrometry is very tedious, and introduces additional errors, and the use of loose resin specimens for spectrometry lowers considerably the sensitivity of the determination and the accuracy of the analysis, as a result of the increase in the standard deviation, associated with the nonuniformity of the particles.

2. The Use of Ion Exchange Papers and Membranes

In XRF analysis, increasing use is now being made of analysis by a thin layer technique, since it makes it possible to avoid matrix effects. Work in which elements are concentrated using paper impregnated with an ion-exchange resin, and different types of filters containing complex-forming groups, is therefore of considerable interest.

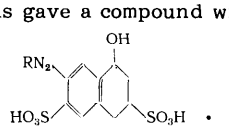
A method of obtaining filters of this kind, capable of concentrating transition and alkaline earth metals, has been described[50]. Chlorodihydroxycellulose (obtained by the reaction of $POCl_3$ with Whatman-41 cellulose) was treated with diethylenetriamine or iminodiacetonitrile, followed by reduction. This gave a chelating ion-exchange filter:



which was used successfully in XRF analysis.

Filters of this type are also available commercially, for example Chelex-100 and Acropore-SN, with diameter 47 mm, containing chelating iminodiacetic acid groups[51]. Thus uranium in ground water has been determined using Chelex-100 [52] and Whatman R-81 [53] filters, and also a filter containing 20% SiO_2, modified by silylation with N-β-ethylaminopropyltrimethoxysilane[54]. The uranium detection limit reached 0.3 μg.

Traces (2.5 ppm.) of Fe, Cu, Zn, Sr, and Hg have been isolated from water using specially prepared cellulose filters[55]. The chromotropic functional group was introduced into the cellulose as follows: *p*-aminophenylcellulose (RNH_2) was first prepared, after which RNH_2 was treated with a mixture of HCl and $NaNO_2$ to give $RN_2^+Cl^-$, to which chromotropic acid was added. This gave a compound with a capacity of 0.2 mmole g^{-1}:



As already noted, ion-exchange filters are being used increasingly in XRF analysis. The number of studies in this field has increased sharply in recent years. The method is used in the analysis of water and in the analysis of various organic and inorganic materials after decomposition. One of the most interesting studies describes the determination of calcium and strontium in mineral waters[56]. The mineral water was passed eight times through a Whatman SA-2 filter impregnated with a cation exchange resin. The XRF spectrum was excited using the ^{109}Cd isotope. The detection limit according to the 3σ criterion is 7×10^{-5}–2×10^{-3}% for calcium, and 5×10^{-6}–2×10^{-4}% for strontium.

Traces of Cr, Fe, Cu, Zn, Sr, Cd, and Ba in surface waters have been determined using Amberlite NR-120 ion-exchange paper[57]. Similar methods have been used to determine Hg in water[58], osmium and ruthenium in the presence of large quantities of Cu, Fe, and Ni[59], the lanthanides[60], gold and silver in metallic copper[61], V, Cu, Fe, and Ni in mineral oils[62], and a number of other elements[63]. It should not be concluded, however, that the combination of ion-exchange separation on a filter with an XRF determination is suitable only for determining cations. The method has been used for the quantitative determination of sulphates[64]; the solution is passed through a filter of SB-2 anion-exchange resin, with subsequent XRF determination of sulphur.

The methodology of a study of the determination of copper and silver in pure lead[65] differs from that of the above studies. To separate Pb, the dissolved specimen is passed through a column of Chromosorb W-HP impregnated with a solution of dithizone in *o*-dichlorobenzene, and the silver and copper ions remaining in solution are concentrated on 2.5 cm diameter discs of SERVA-SB-2 ion-exchange paper as the complexes $[AgI_4]^{3-}$ and $[CuI_4]^{2-}$. Silver and copper are determined by XRF.

Table 2. The use of ion-exchange filters and membranes for preliminary concentration in XRF analysis.

No.	Filter	Material	Elements determined	Refs.
1	Chelex-100	water, pH 7–8	heavy metals	[51]
2	Chelex-100	water	U ($0{,}5 \cdot 10^{-7}$%)	[52]
3	Chelex-100	water, pH 2.5	U (0.3 μg)	[53]
4	Paper impregnated with $AgNO_3$	steel	Se (10 μg)	[66]
5	SB-2	lead	Ag, Cu (0.2 μg)	[65]
6	SB-2	fuel	SO_4^{2-} (1%)	[64]
7	SB-2	water, pH 0.3	Os, Ru	[59]
8	SB-2	water	Hg (1 μg in 50 ml)	[58]
9	Chromatographic paper	water	Cs, Ba, Ln, Ag, Zn, Fe, Hg (10^{-7} g)	[63]
10	Ion-exchange membrane	mineral oils	V, Cu, Fe, Ni (10^{-4}%)	[62]
11	Ion-exchange membrane	copper	Au, Ag (100 μg)	[61]
12	SA-2	metals	Ln (10 μg)	[60]
13	Amberlite HP-120	water	Cr, Fe, Cu, Zn, Sr, Cd, Ba (1–$3 \cdot 10^{-4}$%)	[57]
14	SA-2	water	Ca ($7 \cdot 10^{-5}$%), Sr ($5 \cdot 10^{-7}$%)	[56]
15	Cellulose with the chromotropic group	water pH 4–7	heavy metals (1×10^{-5}%)	[55]
16	Cellulose with amino-groups	water	Ln	[50]

Paper can be impregnated not only with an ion-exchange resin but also simply with solutions capable of absorbing substances liberated as gaseous products. Thus Japanese workers have proposed a method for determining selenium in steels, based on its liberation as H_2Se and fixing on paper impregnated with silver nitrate[66]. When the liberation of H_2Se was complete, the paper was used as the emitter in the XRF determination (see Table 2).

Although the use of ion-exchange filters and membranes is attractive, they generally have a low capacity, which is inconvenient in the analysis of solutions with a large salt background.

IV. COMBINATION OF X-RAY FLUORESCENCE ANALYSIS WITH EXTRACTION

The combination of the XRF determination with concentration by extraction is of interest, because of the speed and simplicity of the extraction concentration. Both liquid extraction and extraction by low-melting organic substances are now used.

1. Liquid Extraction

One of the first studies in this field dealt with the determination of transition metals at concentrations of 10^{-8}–10^{-6}%.[67] The metals were extracted as the diethyldithiocarbamate complexes by carbon tetrachloride. Polystyrene was then added to the extract, and the mixture evaporated on a Mylar film under an infrared lamp. This film was then analysed by XRF.

Later, a more complex method of preparing the specimen was used to determine V, Cr, Mn, Fe, Co, Ni, Cu, and Zn in sea water[68]. The elements to be determined were separated as the pyrrolidinedithiocarbamates by treating with methyl isobutyl ketone, and then transferred to nitric acid solution and sorbed on cellulose powder, which was compressed to form a disc. The reference specimens were prepared similarly from standard solutions. The elements listed could be determined at concentrations of 0.1 μg litre^{-1}.

Micro-quantities of palladium in titanium alloys have been determined by extracting palladium diethyldithiocarbamate with chloroform[69]. The emitter was prepared by impregnating a 15 mm diameter filter-paper disc with the extract. A similar method was used to determine technetium in waste products from nuclear fuel production[70], and uranium and neptunium in metallic plutonium[71].

In the Soviet literature, the determination of micro-quantities of tantalum in technetium solutions[72] and of zirconium and hafnium in heat-resistant alloys[73] by a combination of liquid extraction and XRF determination of the metals in the extract has been described.

Leyden[74] determined phosphorus in natural waters at concentrations of 10^{-7}% using selective extraction by ethyl acetate as molybdophosphoric acid. Phosphorus was determined using the Mo K_α line. This indirect determination of light elements from the emission of heavier elements is opening up a new and promising field in the XRF analysis of light elements.

2. Extraction by Low-Melting Organic Substances

Increasing use is now being made of low-melting organic extracting agents, and solutions of extracting agents in low-melting organic solvents. The combination of high-temperature extraction with XRF analysis of the extract is particularly promising, since when the extraction mixture is cooled, the solid organic phase is obtained directly in a form suitable for spectrometry. This property has been used in the determination of Cr, Fe, Co, Ni, and Cu in fresh water after extraction by molten 8-quinolinol at 98 °C.[75]

One of the most widely used low-melting solvents is naphthalene[76] or its mixtures with other organic substances[77]. The use of naphthalene as extracting agent, however, does

not make it possible to determine elements whose XRF analysis requires a vacuum. Another disadvantage of working with naphthalene is the low viscosity of its solutions, which causes difficulty in the separation of phases with markedly different quantities. It is much more convenient to use as the organic phase a mixture of C_{17}–C_{20} aliphatic acids.

Micro-quantities of Cr, Mn, Fe, Co, Ni, Cu, and Zn have been extracted by a solution of 1-phenyl-3-methyl-4-benzoylpyrazolone-5 in a molten mixture of aliphatic acids[78]. A similar procedure has been used[79] to determine bismuth in various materials with preliminary extraction by dithizone or 2,3,4-trihydroxy-4'-chlorobenzene (sic). Japanese workers have concentrated Co, Fe, Ni, Cu, Zn, Pb, Bi, and Cd by extracting their pyrrolidinedithiocarbamate complexes into molten stearyl alcohol[83]. The chelates of all these metals except iron are transferred quantitatively to the organic phase at pH 5. The extraction of iron is not complete, since its chelates are unstable at high temperatures.

Extraction by low-melting organic substances provides an approach to the solution of the problem of the standardisation and unification of the XRF determination of traces of elements in various natural and industrial materials. The combination of the individual solution of the specimen to be analysed with subsequent extraction by low-melting organic substances and the production of an emitter from the solidified extract makes it possible to obtain a standardised matrix which is independent of the previous history of the substance being determined.

The general questions of the metrology of chemical XRF analysis have been examined in detail[84]. An analysis of the dependence of the relative standard deviation $S_{r,\,c}$ on the concentration $c_{min,\,p}$ showed that preliminary concentration makes it possible not only to lower $c_{min,\,p}$ but also to increase the reproducibility of the results at low concentrations. The use of low-melting extracting agents makes it possible to lower the random and systematic errors in the analysis by eliminating matrix effects and making possible the construction of universal calibration characteristics. If the low-melting extracting agent contains only light atoms, it is possible to reduce to a minimum the effects of absorption and selective excitation. On the other hand, if it is necessary to produce very thin saturated layers, it is possible to use low-melting extracting agents containing heavy atoms, for example bromine. The use of hetero-organic compounds with a known concentration of the reference element makes it possible to increase considerably the accuracy of the determination using an internal standard.

It should be emphasised again that chemical XRF analysis is finding increasing application in the analysis of water and in the analysis of other most varied materials (steels, alloys, and organic and biological materials). In the analysis of solid substances, concentration is preceded by solution.

The choice of the optimum method of concentration is determined by the conditions of the analysis, interfering elements, and the accuracy and sensitivity required in each specific case.

As already noted, an advantage of the methods described, compared with traditional non-destructive XRF methods, is that the preliminary decomposition and concentration of the specimen makes it possible to eliminate the corrections for matrix effects and non-uniformity of composition and particle size. On the other hand, the combination of chemical methods of concentration with the XRF determination of elements in the concentrates makes it possible to avoid the restrictions associated with the chemical nature of the elements being determined (the superposition of colours in photometry, etc.), and does not require preliminary separation of the elements.

Thus the combination of XRF with various chemical and physicochemical methods of concentration is a promising development in the determination of traces of elements.

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Chromatography in a Gas-Colloid System

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The results of the study of colloidal systems based on highly dispersed adsorbents and colloidal solutions of polymers as universal stationary phases for gas chromatography have been analysed. Particular attention has been paid to the regular features of retention on colloidal sorbents and the estimation of their selectivity and thermal stability. Possible fields of analytical application (the separation of mixtures of organic and organometallic compounds, trace analysis, and capillary chromatography) have been examined.
The bibliography contains 70 references.

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I. INTRODUCTION

In practical gas chromatography (GC), increasing use is being made of sorbents combining the properties of solvents and adsorbents. The use of sorbents operating under intermediate adsorption–absorption conditions extends gas-chromatographic analysis chiefly by making it possible to control the selective properties of the chromatographic packing by changing the relationship between the contributions of solution and adsorption in the overall retention. The use of sorbents with controllable selectivity makes it possible to reduce considerably the range of stationary phases (SP) for gas chromatography.

Sorbents of the intermediate type include: 1) macroporous carbon adsorbents, modified by liquid phases, of the Carbochrome or Carbopak type, 2) macroporous silica adsorbents, modified by liquid phases, of the Silochrome or Spherosil type, 3) porous polymers, modified by liquid phases, of the Porapak or Polysorb type, 4) adsorbents with stationary liquids chemically bound on the surface (graft sorbents of the Durapak type), 5) organic derivatives of clays (Bentones) on an inert solid carrier, 6) liquid crystals on an inert solid carrier, and 7) colloidal systems on an inert solid carrier.

Adsorption–absorption chromatography using modified Silochromes and graphitised carbon black[1-3], the use of modified polymers in gas chromatography[4], problems of chromatography on Bentone columns[5-7], analytical and physicochemical aspects of chromatography in a gas–liquid crystal system[8], and graft sorbents[9] have already been reviewed.

The modification of adsorbents by a liquid phase makes it possible to control the selectivity, eliminates the asymmetry of the peaks due to polar substances, and in the case of carbon black increases the mechanical strength of the sorbent. Usually, with increase in the quantity of stationary phase on the adsorbent carrier, the efficiency increases up to the formation of a monolayer, after which it decreases as a result of a decrease in the rate of mass exchange[2]. This restricts the range of the selectivity of modified adsorbents suitable for practical application, and naturally reduces the range of analytical problems that can be solved using a given adsorbent–modifier system.

Bentones belong to the class of intermediate sorbents because of the mixed mechanism of the interaction of the sorbates with adsorption centres on the one hand and with organic groups on the other. Since liquid crystals show simultaneously (within a short temperature range) the properties of both liquids and solids, they also act as intermediate sorbents. It should be noted that both Bentones and liquid crystals, which have a high selectivity with respect to structural isomers, have a moderate group selectivity.

Colloidal systems (colloids) in the most general sense are systems in which substances are subdivided to give very small particles (10^{-4}–10^{-7} cm). A necessary condition for the colloidal state of a system is the insolubility of one phase in the other. The existence of a physical surface between the phases, that is the heterogeneous character of colloids, represents the basic difference between them and true homogeneous solutions. From the molecular-kinetic properties typical of polymer solutions (low osmotic pressure, little diffusion of the macromolecules, and their inability to pass through a semi-permeable partition in dialysis), they must be classified as colloidal systems. This similarity is related to the fact that the dimensions of the particles, which determine the properties of the solutions of both types, are similar to one another and much greater than those of ordinary molecules.

A chromatographic study of a binary squalane–stearonitrile mixture[10] confirmed the suggestion that micelles exist in mixtures of non-polar liquids with nitriles. Thus these and similar binary liquid phases are colloidal.

Of the wide range of types of colloidal system, classified according to the state of aggregation of the dispersed phase and the dispersion medium, the systems formed by a solid and an organic liquid, that is organosols and gels of highly dispersed adsorbents and polymers, are of greatest interest from the present viewpoint. The use of these systems as sorbents is attractive because it is possible, by changing the composition, to vary smoothly the sorption characteristics of the packing in a range from the properties of the liquid to the properties of the solid, which is difficult in the classical form of gas chromatography on modified adsorbents.

If organic derivatives of clays are regarded as one-dimensional colloids in view of the "colloidal" dimensions of the particles in one of three directions[11], then Bentones were essentially the first colloidal systems to find gas-chromatographic application. Bentones mixed with liquid phases form stable colloidal systems[12]. It has been suggested[13] that on

treatment with a silicone oil, the crystal lattice of Bentone-34 is deformed, and the mixture becomes a thixotropic gel. Modified Bentones have been widely used in the analysis of aromatic isomers[5-7].

Colloidal systems can be obtained by introducing an appropriate filler into viscous organic liquids. The first examples of these stationary phases were silicone greases[14]. The influence of the silica fillers in high-vacuum silicone grease on the value of the retention has been studied[15]. Pecsok and Vary[16], working with dispersions of metallophthalocyanines in silicone oil, were among the first to demonstrate clearly the advantages of the directed use of adsorption effects in gas–liquid chromatography. It subsequently appeared appropriate to carry out detailed studies of the chromatographic properties and analytical possibilities of colloidal sorbents.

The present review examines two types of colloidal system as SP for gas chromatography—colloidal solutions of polymers and colloidal systems based on highly dispersed adsorbents. Studies carried out by the authors have shown that these stationary phases make it possible to control the selectivity of chromatographic separation over a wide range, and hence to solve a large number of analytical problems.

II. REGULAR FEATURES OF RETENTION ON COLLOIDAL SORBENTS

1. Preparation of Colloidal Sorbents

The method of preparing sorbents with colloidal polymer solutions as stationary phases is protected by a patent[17] and has been described in a number of papers[18-21]. Dispersions of macromolecular compounds corresponding to the colloidal state were obtained by the aggregation of the macromolecules in the solution by the introduction of a high-boiling liquid modifier. When the solvent was evaporated and an inert carrier added to the heated mass (80–100 °C), the solid surface was covered by aggregates of molecules of the colloidal system. Polyvinyl alcohol (PVA), polystyrene (PS), and low-pressure polyethylene (PE) were used as polymeric components. Polyethylene glycol-400 (PEG-400), dinonyl phthalate (DNP), and squalane were used as modifiers.

Ultrasonic dispersal† has been used to prepare colloidal SP based on highly dispersed adsorbents[22-26]. The Aerosil (highly dispersed silicon dioxide) or PM-15 grade carbon black was introduced into solutions of the organic liquid squalane, PEG-400, PEG-40000, polymethylsiloxane (PMS-100), or polymethylphenylsiloxane (PMPS), after which the prepared suspension was deposited on inert solid carriers. Since the particle size of the fillers used lay in the colloidal range ($\sim 10^{-5}$–10^{-6} cm), the systems based on them are colloidal. An apparatus for continuous vigorous shaking has been used to increase the thermal stability of stationary phases by adding solid highly dispersed binding agents of the Aerosil or graphitised carbon black type[27]. There is no difference between the filling of capillary columns by colloidal stationary phases[28] and that in ordinary gas–liquid chromatography.

†A similar method has been used to obtain stable coatings in capillary chromatography (see section VI).

2. Influence of the Composition of the Colloidal Stationary Phase on the Retention of Polar and Non-polar Compounds

A necessary condition for the successful gas-chromatographic analysis of a mixture is the correct choice of sorbent. The use of binary or multiple systems makes it possible to vary smoothly the selectivity of the chromatographic separation and hence to carry out a directed search for the sorbent with the optimum properties. The dependence of the elution characteristics of the components of the mixture being analysed on the composition of the combined stationary phase provides a basis for the solution of this problem. For the usual mixed liquid phases, these relationships in most cases are linear. A characteristic feature of colloidal systems is the presence of breaks and extremal points on the plots of $\lg V_g$ against composition (V_g is the specific retention volume). Anomalies in the retention process are due to specific interaction between the components of the system, and also adsorption factors.

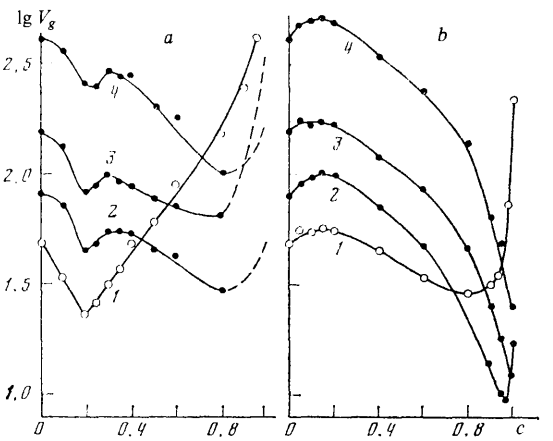


Figure 1. Dependence of the retention on the composition of colloidal SP; PEG-400–Aerosil (*a*) and PEG-400–carbon black (*b*); *1*) nonane, *2*) benzene, *3*) ethanol, *4*) nitromethane[22,25].

The dependence of the retention on the composition of colloidal SP containing highly dispersed adsorbents is given in Fig. 1 (*c* is the mass fraction of the adsorbent). The curves corresponding to the retention of alkanes on columns containing a PEG-400–Aerosil system have a minimum at $c = 0.2$.[22,26] This composition corresponds to the conversion of the colloid from the free-dispersed state (sol) into the bound-dispersed gel-like state. This agrees with data obtained by the workers who developed the Soviet Aerosil[29], and is confirmed by electron-microscope studies[26]. In addition to this minimum at $c = 0.2$ for polar compounds, there is another deeper minimum corresponding to $c = 0.8$. At this component ratio, the contribution of solution is appreciable. A higher concentration of Aerosil corresponds to a sharp increase in the retention volume, due to adsorption on the gas–Aerosil surface with the production of asymmetric peaks. The position of the extremal points on the $\lg V_g$–composition curves for the PEG-400–carbon black system[25] corresponds to the same

component ratio as in the PEG-400–Aerosil system. The colloidal conversion is accompanied by the maximum retention for this system, however.

Thus the form of the extremal point is determined by the nature of the interaction between the components of the colloidal stationary phase, since the glycol is able to form hydrogen bonds with the Aerosil, whereas its interaction with the carbon black involves chiefly non-specific forces. Fig.1 also shows that by introducing a highly dispersed carrier into the stationary phase, it is possible to change smoothly the retention of the substances being analysed, as far as a change in the order of their elution.

For the organic PS–squalane system (Fig.2), the retention characteristics pass through a maximum at equal proportions of the modifier and the polymer, indicating an interaction between the components of the colloidal stationary phase at this component ratio. The extremal points on the graph giving the dependence of the retention on composition for the PE–PEG-400 system are not so sharp as those for the sorbent based on polystyrene. Here also, however, change in the ratio of the components of the stationary phase can be used to control the selectivity of the column in the analysis of organic compounds of various classes. The sharp increase in the retention of polar sorbates on going from the pure polymer to the mixture with a small quantity of the glycol is apparently due to the influence of the adsorption factor[30].

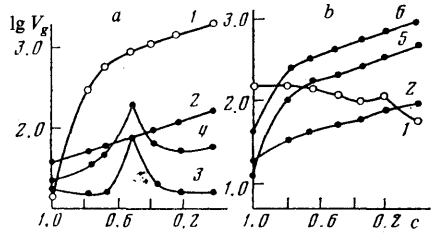


Figure 2. Dependence of the retention on the composition of colloidal SP; PS–squalane (*a*) and PE–PEG-400 (*b*); *1*) nonane, *2*) benzene, *3*) ethanol, *4*) methyl ethyl ketone, *5*) nitromethane, *6*) pyridine[18,19].

In a study of the absolute retention of benzene, allyl iodide, and chlorobenzene on the mole fraction (x_A) of strearonitrile in squalane, maxima were observed at x_A = 0.1–0.2.[10] In the opinion of the authors cited, this was due to the formation of micelles in this system.

Thus for practically all colloidal systems, the plot of the logarithm of the retention volume against the quantitative ratio of the phases is non-linear. The presence of breaks and extremal points on these curves is determined by the nature of the interaction between the components of the system, and adsorption factors. Change in the composition of the colloidal sorbent over a wide range makes it possible to control the sorption characteristics of the chromatographic packing.

3. Influence of Temperature on Retention by Colloidal Stationary Phases

The temperature of the column (T), together with the composition of the sorbent, provides an efficient means of controlling the selectivity of a chromatographic separation. This is particularly true of systems containing polymers or liquid crystals, that is materials which change their phase state in the range of temperatures used in gas-chromatographic analysis.

It is known[31] that

$$\lg V_g = A + B/T \quad . \qquad (1)$$

The coefficient A is related to the entropy of sorption, and the coefficient B is the enthalpy component. A change in the nature of the sorption in the range of the temperatures of the phase transformation of the polymer for polar and non-polar sorbates leads to a change in the absolute values of the constants A and B in Eqn.(1), leading to distortion of the plot of the logarithm of the retention volume against the reciprocal of the absolute temperature (Fig.3).[21] These distortions are observed chiefly for non-polar or weakly polar compounds (alkanes and aromatic hydrocarbons). This indicates that the modifier makes the predominant contribution to the retention of polar compounds (PS–PEG-400 system) and that there is no specific interaction between sorbates and the PE–squalane sorbent. For colloidal solutions of polystyrene and polyvinyl alcohol in squalane, the opposite picture is observed. Increase in the concentration of the polymer in the binary stationary phase leads to more clearly defined breaks on these curves for compounds whose retention is determined by the polymeric component.

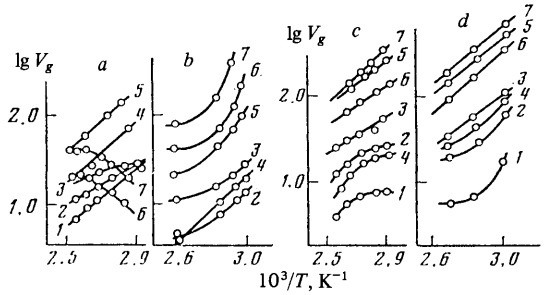


Figure 3. Plot of the retention against the reciprocal of the absolute temperature of the column; *a*) PS–PEG-400 (c = 0.67), *b*) PE-squalane (c = 0.2), *c*) PS–squalane (c = 0.4), *d*) PVA–squalane (c = 0.6); *1*) ethanol, *2*) methyl ethyl ketone (MEK), *3*) benzene, *4*) nitromethane, *5*) pyridine, *6*) n-nonane, *7*) n-decane[18,19].

A change in the selectivity of the column in the range of the temperatures of the phase transformation is particularly characteristic of the PS–PEG-400 system. When polystyrene changes from the vitreous to the highly elastic state (~100 °C), the retention of alkanes increases to such an extent that the peak of nonane is "displaced" into the middle of the chromatogram, passing in front of ethanol, methyl ethyl ketone, nitromethane, and pyridine. Thus the use of colloidal solutions of polymers as stationary phases makes it possible to control the selectivity of the chromatographic column in the temperature range of the change in the phase state of the polymer without replacing the sorbent.

A study of the temperature dependence of the retention for the colloidal stationary phases PEG-400–Aerosil and squalane–Aerosil# established[22,26] that for all sorbates they are linear,

#Here and subsequently, the squalene–Aerosil and squalane–carbon black systems are systems with the addition of 15% PEG-400 relative to the mass of Aerosil and 1.5% relative to the mass of carbon black.

since the phase state of the components does not change in the temperature range studied. The plot of the retention volume against the reciprocal of the temperature for a PEG-40000–Aerosil sorbent has been studied[24,26]. The graphs show breaks in the absence of the adsorbent, and at a relative concentration of the adsorbent $c = 0.1$ and 0.2. As with polymer solutions, the deviations from the linear relationship characterise the change from the adsorption of the substances being analysed on the surface of the solid polymer to solution, due to the diffusion of the molecules into the depth of the liquid polymer film, leading to an increase in the capacity of the sorbent. The increase in retention takes place before equilibrium absorption is reached. As the Aerosil is added to the polymer, the inflection on the retention curve gradually decreases, and it disappears completely at $c = 0.3$. An interesting feature is that the sorbent with this composition shows the strongest specific adsorption properties[24].

4. Influence of Adsorption Factors on Retention by Colloidal Stationary Phases

As already noted, the marked deviation from linearity shown by the dependence of the retention characteristics of the sorbates on the composition of the binary colloidal phase may be due to adsorption phenomena. Retention in a gas–colloid system is determined by solution in the liquid phase (the dispersion medium of the colloid), adsorption on the surface of the colloidal particles of the polymer or adsorbent (the disperse phase of the colloid), and also adsorption at the boundaries between the phases. The influence of these factors on retention has been studied[20,21,23,26].

Since the stationary phases were deposited on fairly inert silanised carriers in quantities of more than 10%, adsorption at the gas–solid carrier and liquid–solid carrier boundaries could be neglected. For the description of the adsorption effects on colloidal organic phases[20,21], an equation was proposed, relating the specific retention volume (V_g) to the distribution and adsorption constants

$$\frac{V_{g,p}}{s} = \frac{\Gamma}{s}\frac{W}{g + g_c} + \Gamma_1 \qquad (2)$$

where $V_{g,p}$ is the specific retention volume per gram of packing, $cm^3\ g^{-1}$; s the surface area of 1 g of the colloid, cm^2; Γ the coefficient of sorption by the colloid, $(g\ cm^{-3}/g\ cm^{-3})$; Γ_1 the coefficient of adsorption on the gas-colloid surface, cm; W the volume of colloidal solution in the column, cm^3; g its mass, g; and $g + g_c$ the mass of packing, g.

Since the coefficients of adsorption of polar and non-polar sorbates at the gas–colloid surface for systems containing highly dispersed adsorbents are negligible[23], the sorption by these sorbents was calculated using the equation[26]:

$$V_{g,p} = \Gamma\frac{W}{g + g_c} \quad . \qquad (3)$$

Eqns.(2) and (3) are applicable for systems containing a small quantity of a disperse phase and consisting of colloidal solutions or sols. The quantity Γ in Eqn.(2) characterises the adsorption by the colloidal particles of the polymer[20,21]:

$$\Gamma W/(g + g_c) = \Gamma_m W_m/(g + g_c) + \Gamma_m\Gamma_s s_{pl,p} \qquad (4)$$

where W_m is the volume of the modifier in the column, cm^3; $s_{pl,p}$ the surface area of the colloidal particles of the polymer, calculated for 1 g of packing, $cm^2\ g^{-1}$; Γ_s the coefficient of adsorption on the surface of the colloidal particles, cm; and Γ_m the distribution coefficient between the pure modifier and the gas phase, $(g\ cm^{-3})/(g\ cm^{-3})$.

Eqn.(4) gives

$$\frac{\Gamma}{\rho}\frac{\Pi}{\Pi + 100} = \frac{\Gamma_m}{\rho_m}\frac{1 - c}{1 + 100/\Pi} + \Gamma_m\Gamma_s s_{pl,p} \qquad (5)$$

where Π is the percentage impregnation of the solid carrier by the colloid; ρ the density of the colloid, $g\ cm^{-3}$; ρ_m the density of the modifier, $g\ cm^{-3}$; and c the mass fraction of the polymer in the mixture with the modifier.

The relationship

$$\frac{\Gamma}{\rho} = \Gamma_m\left[\frac{1 - c}{\rho_m} + \Gamma_s\left(1 + \frac{100}{\Pi}\right)s_{pl,p}\right] \qquad (6)$$

can then be brought to an equation of the form

$$\frac{\Gamma}{\rho} = \Gamma_m\left[\frac{1 - c}{\rho_m} + \Gamma_s s_{pl,pl}c\right] \qquad (7)$$

($s_{pl,\,pl}$ is the surface area of the particles, calculated for 1 g of polymer, $cm^2\ g^{-1}$).

If Γ_m is known from the data obtained using the pure modifier, it is possible to calculate $\Gamma_s s_{pl,\,pl}$, that is the adsorption by 1 g of polymer present in the colloidal state.

With increase in the proportion of the dispersed phase, the colloidal solution is converted into a gel-like state. The system loses its flow properties as a result of the agglomeration of the micro-particles to give a coagulation structure. The overall surface area of the sorbent increases. In the general case it may be assumed that the retention of the compounds being analysed for these systems is determined by the sorption by the gel. Thus

$$V_{g,p} = \Gamma_g s_g \qquad (8)$$

where Γ_g is the coefficient of sorption by the gel, cm; and s_g the surface area of the gel for 1 g of packing, $cm^2\ g^{-1}$.

The contributions of solution and adsorption to the total retention on organic colloidal sorbents can be estimated from Eqn.(4).[20] When colloidal systems containing highly dispersed adsorbents are used, part of the modifier does not take part in the sorption process, but is used up in suppressing the active centres of the solid carrier. Thus with allowance for this characteristic feature of these systems,

$$V_N = \Gamma_m(W_m - W'_m) + \Gamma_m\Gamma_a s_a \qquad (9)$$

where V_N is the effective retention volume, cm^3; Γ_a the coefficient of adsorption on the surface of the adsorbent in the colloidal state, cm; s_a its surface area, cm^2; and W'_m the volume of the modifier not taking part in the sorption process, cm^3.

The proportion of the modifier W'_m corresponds to the ratio of the components of the system at which the change to adsorption on the surface of the adsorbent takes place. This change corresponds to the retention minima on the plots of $\lg V_g$ against composition in the range of high values of c. Thus for the PEG-400–Aerosil system (Fig.1), $W'_m = 0.25g_a/\rho_m$ (g_a is the mass of highly-dispersed adsorbent in the column for the composition $c = 0.8$).

It can be shown that $g_a = W_m\rho c/(1 - c)$, so that $W'_m = 0.25W_m c/(1 - c)$. By analogy with the PEG-400–Aerosil system, for the PEG-400–carbon black system $W'_m = 0.015W_m c/(1 - c)$.

The use of these relationships for the quantitative estimation of the factors determining retention showed[20,21,26] that change in the composition of the colloidal stationary phases, and in the case of polymer solutions change in the temperature of the column, leads to a change in the ratio between the contributions of adsorption and absorption forces to the overall retention. This makes it possible to control the selectivity of separation and elution times of substances being analysed.

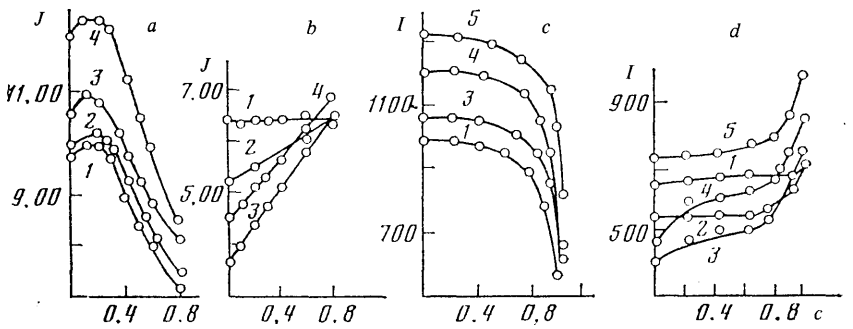


Figure 4. Dependence of the retention indices on the composition of colloidal SP: *a*) PEG-400–Aerosil, *b*) squalane–Aerosil, *c*) PEG-400–carbon black, *d*) squalane–carbon black; *1*) benzene, *2*) MEK, *3*) ethanol, *4*) nitromethane, *5*) pyridine[22,25].

III. SELECTIVITY OF COLLOIDAL STATIONARY PHASES

The range of stationary phases for GC on the world market includes more than 900 products. In spite of this, cases are frequently encountered where no known phase gives the required separation. These "selectivity gaps" are observed particularly in the selection of sorbents for the analysis of multi-component mixtures. The choice of sorbent is facilitated considerably by using different kinds of combined stationary phase, in particular colloidal systems.

1. Indices of Retention on Colloidal Sorbents

A convenient characteristic of the selectivity of a stationary phase towards a definite class of compound is provided by the logarithmic retention indices (Kovats indices) of a given substance *I* belonging to this class[32,33]. Its linear analogue *J* [33,34] is simpler in calculations. These data can be used to classify sorbents according to their polarity, and also to estimate the range of change in selectivity using combined sorbents.

Figs.4*a* and 4*b* [22,25] give the dependence of the linear retention index on the composition of colloidal stationary phases based on Aerosil. For the PEG-400–Aerosil system, the *J* curves for all the sorbates studied show maxima at the composition corresponding to the conversion of the sol to the gel. For the squalane–Aerosil system, the dependence of *J* on *c* is practically linear. The relative error in the determination of the linear retention indices did not exceed ±0.04 index unit. As a result of the change in the nature of the interaction on going from the PEG-400–Aerosil sorbent containing 20% adsorbent to the sorbent containing 80% adsorbent, the linear retention index of benzene, methyl ethyl ketone, and ethanol can be changed by 3 units, which corresponds to 300 units of the Kovats index, and that of nitromethane can be changed by 3.7 units (370 units). On pure squalane, ethanol is eluted before butane, and on a squalane–Aerosil sorbent with $c = 0.8$ it is eluted after hexane.

The dependence of the logarithmic retention index on the composition of stationary phases containing carbon black has been studied[25,26] (Figs.4*c* and 4*d*). In contrast to the PEG-400–Aerosil system, the change from the sol to the gel for the colloid containing carbon black is not accompanied by a maximum on the graph, since the interaction of polar and non-polar sorbates with the non-specific adsorbent involves dispersion forces. The greatest decrease in the retention indices begins at a carbon black concentration of 60% in its mixtures with the glycol. A different picture is observed for the squalane–carbon black system. Thus for ethanol and nitromethane, substances which tend to undergo strong specific interactions with a carbon black surface treated with a small quantity of glycol, breaks are observed on the curves at a low concentration of a highly dispersed filler. On going from the sorbent with $c = 0.2$ to the sorbent with $c = 0.985$ in the PEG-400-carbon black system, the retention indices can be changed by 280 units for benzene, by 300 units for ethanol, and by 370 units for nitromethane. On squalane, the retention index of methyl ethyl ketone is 140 units greater than that of ethanol, and on squalane containing 90% modified carbon black, the retention index of ethanol is 16 units greater than that of methyl ethyl ketone.

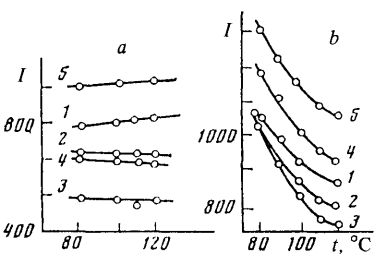


Figure 5. Dependence of the retention indices on the column temperature; *a*) PS–squalane ($c = 0.5$); PS–PEG-400 ($c = 0.5$).[21] See Fig.4 for numbering of sorbates.

Fig.5 [21] gives the temperature dependence of the Kovats indices of standard sorbates on polymeric colloidal phases. The greatest temperature "displacement of the indices" is observed for the PS–PEG-400 system. In this case the index of benzene, for example, in the range 80–100 °C decreases from 1005 units to 870 units, due to the increase in the retention of alkanes in the region of the phase transformation of polystyrene. For other colloidal solutions of polymers, the changes in *I* with change in the column temperature are slight. Thus for the PS–squalane system in the same temperature range, it changes by only 10 units (from 690 to 700).

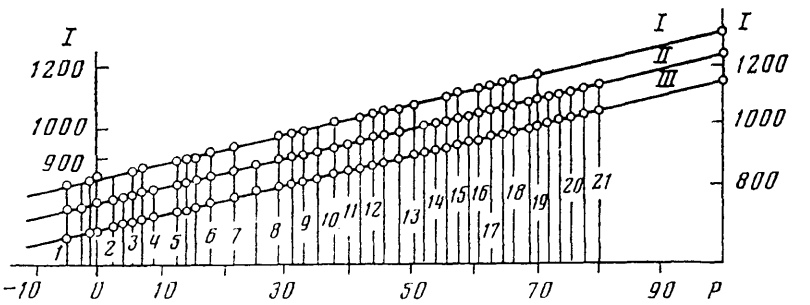


Figure 6. Dependence of the retention indices of ethylbenzene (*I*), toluene (*II*), and benzene (*III*) on the conditional chromatographic polarity[20,21]. For the numbering of the phases see Table 1.

2. Conditional Chromatographic Polarity of Colloidal Sorbents

The selection of the sorbent for the separation of a specific pair of components or a mixture of substances belonging to the same class is simplified considerably if its conditional chromatographic polarity *P*, a characteristic of the phase determined by the presence of groups other than alkyl groups, is known. According to Rohrschneider[35], who first proposed this approach to the selection of sorbents and their classification according to polarity, *P* is given by the expression

$$P = \frac{\lg r_2 - \lg r}{\lg r_2 - \lg r_1} \qquad (10)$$

where r_1 and r_2 are the ratios of the retention volumes of butadiene and butane on squalane ($P = 0$) and on β,β'-hydroxydipropionitrile ($P = 100$), and r is the corresponding ratio on the sorbent being studied.

The relative retention can be replaced by the retention indices for, for example, aromatic hydrocarbons[36]. In this case, the graphical expression of the conditional chromatographic polarity involves plotting *P* against the retention index. These plots can be used to predict the retention times of the substances being analysed and to select a sorbent with the optimum selectivity. Fig.6 gives the graph[20,21] for determining the conditional chromatographic polarity of colloidal solutions of polymers. The position of the point corresponding to the stationary phase on the abscissa was determined from the retention indices of benzene, toluene, and ethylbenzene. Table 1 gives colloidal systems in order of increasing conditional chromatographic polarity, with the column temperatures, composition, and percentage impregnation.

The change in the conditional polarity with change in the percentage impregnation of the carrier is apparently related to the sorption of the substances being analysed on the surface of the colloidal particles. The selectivity of colloidal binary phases may also be changed under the influence of the temperature factor, and if vitrification of the less polar component takes place, the decrease in its sorptive capacity leads to an increase in the overall polarity of the colloidal phases.

Fig.6 and Table 1 show that, using only six components (three polymers and three stationary liquids), it is possible, by varying their qualitative and quantitative composition, the percentage impregnation of the carrier, and the column temperature, to obtain a fairly wide range of conditional chromatographic polarity (from −5 units to 80 units). The smooth change in the properties of the colloidal systems based on polymers makes it possible to select the required phase for the solution of a specific analytical problem.

Table 1. Dependence of the conditional polarity (*P*) of colloidal polymer phases on the column temperature (*t*), the composition of the stationary phase (*c*), and the percentage impregnation (П).[20]

Phase No.	System	*t*, °C	*c*	П	*P*
1	PE	60	1.00	15	−5
2	PVA in DNP	60	0.8	15	2
3	PE in DNP	120	0.8	25	5
4	PE in DNP	60	0.4	15	9
5	PS in squalane	120	0.5	15	13
6	PES in DNP	100	0.6	25	17
7	PE in DNP	100	0.2	15	21
8	PS in DNP	100	0.5	25	29
9	PS in DNP	120	0.6	25	33
10	PE in PEG-400	150	0.3	15	38
11	PE in PEG-400	60	0.3	15	40
12	PS in PEG-400	120	0.8	25	43
13	PVA	100	1.00	15	50
14	PS in PEG-400	100	0.67	15	54
15	PS in PEG-400	100	0.67	30	57
16	PS in PEG-400	120	0.3	15	60
17	PS in PEG-400	100	0.5	30	62
18	PS	100	1.00	15	66
19	PEG-400	100	1.00	15	70
20	PS in PEG-400	80	0.5	30	76
21	PS in PEG-400	80	0.8	30	80

3. Rohrschneider's Polarity Factors for Colloidal Sorbents

Polarity factors have recently been used to characterise the selective properties of sorbents. These factors represent the differences in the retention indices ΔI of standard sorbates of different chemical character on columns with the stationary phase being studied and a non-polar liquid, for example squalane. The Rohrschneider polarity factors[37], that is the values of $\Delta I/100$ for benzene (*x*), ethanol (*y*), methyl ethyl ketone (*z*), nitromethane (*u*), and pyridine (*s*), have been calculated for the colloidal sorbents studied[20–22, 24–26] (see Table 2). These quantities make it possible to characterise in more detail the intermolecular interactions between the sorbent and the substance being analysed, and the set of values of the polarity factors provides as it were a sorbent "specification", which makes it possible to evaluate

its suitability for solving a particular separation problem. The values of the polarity factors and the overall conditional polarity of colloidal organic systems depend on the composition of the stationary phase, the percentage impregnation of the solid carrier, and the column temperature (see also Fig.7). The nature of the change in the polarity coefficients is on the whole analogous to that of the change in the overall conditional polarity (P). The change in the polarity coefficients with change in the percentage impregnation of the carrier characterises the relative contribution of adsorption and absorption factors to the retention of the corresponding standards, compared with the relative contribution of these factors to the retention of alkanes (Fig.7).

Table 2. Polarity factors of colloidal systems based on polystyrene at 100 °C and П = 25%.

System	Solutions in PEG-400					Solutions in squalane			
c	0.2	0.3	0.5	0.67	0.8	0.2	0.5	0.6	0.8
x	3.50	3.36	2.98	2.82	2.56	0.16	0.49	0.70	0.72
y	6.31	5.94	5.16	4.50	3.93	0.60	0.98	1.20	1.47
z	4.43		3.69	3.37	3.07	0.35	0.83	1.00	1.15
u	7.12	6.76	5.95	5.48	4.79	0.55	1.35	1.80	1.84
s	5.65	5.28	4.52	4.28	3.66	0.58	1.07	1.37	1.51

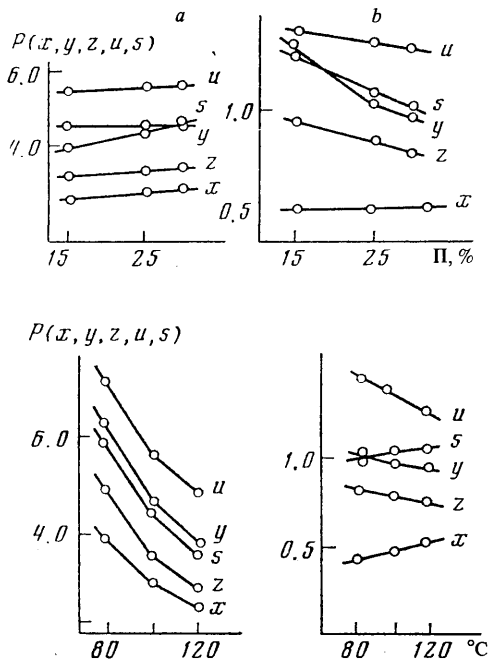


Figure 7. Dependence of the polarity factors of colloidal SP on the percentage impregnation and the column temperature: *a*) PS–PEG-400 (c = 0.67); *b*) PS–squalane (c = 0.5).[21]

The relationships given in Fig.7 can be used to select the optimum conditions for separating components of different classes. For example, to achieve the most selective separation of amines and aromatic hydrocarbons on colloidal solutions of PS in PEG-400, it is necessary to work at low column temperatures and maximum impregnation of the carrier by the liquid phase. To separate amines from nitromethane, the opposite relationship in these experiment parameters is preferred, since this case is characterised by the greatest difference in the polarity factors x and s, which play the most important role in the separation of components of these classes.

Table 3 gives the values of the polarity factors for colloidal stationary phases containing highly dispersed adsorbents. The sorbents studied are arranged in order of increasing constant x, the most universal characteristic of chromatographic polarity.

Table 3. Polarity factors of colloidal systems based on highly dispersed adsorbents[26].

System	c	x	y	z	u	s
Squalane-Aerosil	0.2	0.01	0.64	0.22	0.61	—
Squalane-carbon black	0.1	0.01	0.71	0.21	0.91	0.36
Squalane-carbon black	0.2	0.01	0.97	0.24	1.24	0.45
Squalane-carbon black	0.6	0.04	1.46	0.33	1.63	0.72
Squalane-Aerosil	0.4	0.10	1.36	0.43	1.17	—
Squalane-Aerosil	0.6	0.14	2.12	0.62	1.83	—
Squalane-Aerosil	0.8	0.20	2.83	1.08	2.38	—
Squalane-carbon black	0.9	0.24	2.45	0.82	2.76	1.36
PEG-400-Aerosil	0.8	0.61	4.23	2.07	4.00	—
PEG-400-carbon black	0.985	0.62	3.79	1.94	3.95	2.59
PEG-400-carbon black	0.9	1.59	4.91	2.77	5.29	4.44
PEG-400-Aerosil	0.6	1.84	5.20	3.01	5.46	—
PEG-400-Aerosil	0.4	2.90	6.23	4.09	6.78	—
PEG-400-carbon black	0.6	2.95	6.44	3.94	7.09	5.73
PEG-400-carbon black	0.2	3.41	6.80	4.43	7.56	6.21
PEG-400-Aerosil	0.2	3.61	6.96	4.87	7.60	—

Table 4. Standard and colloidal stationary phases based on highly dispersed adsorbents, having similar polarity factors[26].

SP	x	y	z	u	s
Squalane-Aerosil (0.2)	0.01	0.64	0.22	0.61	—
Silicone SE-30	0.16	0.20	0.50	0.85	0.48
Silicone OV-1	0.16	0.20	0.50	0.85	0.48
Silicone OV-101	0.16	0.20	0.50	0.85	0.48
Armin 2 HT	0.24	0.96	0.29	0.51	0.36
Silicone DC 560 (F 60)	0.31	0.49	0.82	1.08	0.83
Apiezon L	0.32	0.39	0.25	0.48	0.55
Squalane-carbon black (0.1)	0.01	0.71	0.21	0.91	0.36
SP-400	0.83	0.49	0.82	1.08	0.83
Armin 2SD	0.35	0.45	0.37	0.57	1.03
Squalane-carbon black (0.2)	0.01	0.97	0.24	1.24	0.45
Silicone 0-3	0.42	0.81	0.85	1.52	0.89
Armin SD	0.44	1.06	0.79	1.36	0.78
Squalane-Aerosil (0.8)	0.20	2.83	1.08	2.36	—
Fluorolube GR 362	0.51	3.16	2.48	2.51	4.00
Bis(2-ethylhexyl) sebacate	0.73	1.65	1.15	2.20	1.24
Chalkomide M-18	0.78	2.76	1.36	2.69	1.47
Di-isodecyl phthalate	0.83	1.65	1.43	2.53	1.54
Celanised ester No. 9	0.83	1.75	1.28	2.36	1.46
Algaterg T	0.89	3.18	—	2.41	2.30
Squalane-carbon black	0.24	2.45	0.82	2.76	1.36
Dinonyl phthalate	0.84	1.76	1.48	2.70	1.53
STAP	0.89	2.56	1.64	2.44	2.35
PEG-400-carbon black (0.9)	1.59	4.91	2.77	5.29	4.44
Tween 80	2.14	4.20	2.78	5.20	3.65
Bis(2-methoxyethyl) adipate	2.21	4.07	3.16	5.41	3.67
PEG-400-Aerosil (0.4)	2.90	6.23	4.02	6.78	—
Igepal CO-990	2.94	5.12	3.59	6.64	4.67
Chiproz SP-80	2.96	5.57	4.22	6.53	5.91
Ethylene glycol isophthalate	3.00	4.76	4.10	6.51	5.17
PEG-400-carbon black (0.6)	2.95	6.44	3.94	7.09	5.73
MER-21	3.16	5.28	3.78	7.04	5.07
FFAP	3.21	5.79	4.11	7.17	6.45
Carbowax-4000	3.22	5.46	3.86	7.15	5.17
PEG-400-carbon black (0.2)	3.41	6.80	4.43	7.56	6.21
Ethylene glycol adipate	3.43	5.46	4.52	7.11	6.00
Phenyldiethanolamine succinate	3.61	6.24	4.70	7.24	6.32
MER-2	3.67	5.27	4.54	7.10	5.88

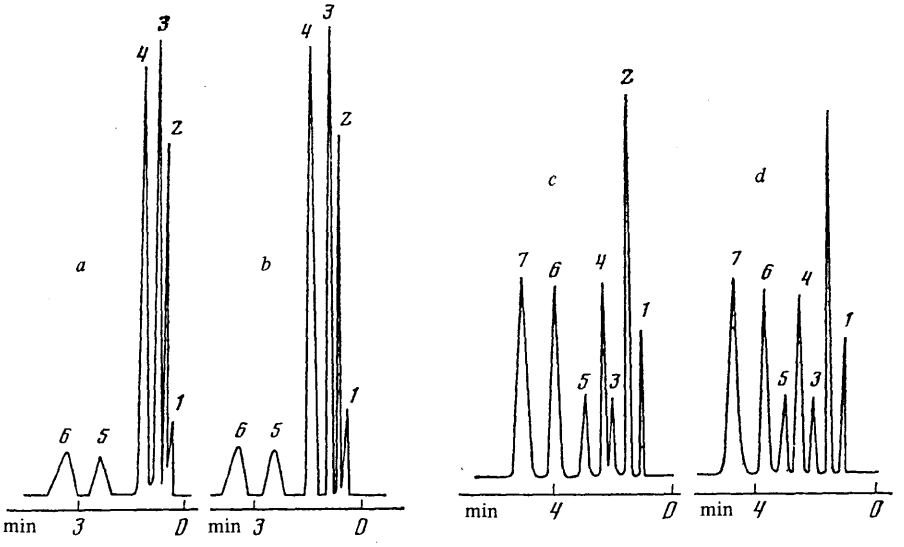


Figure 8. Chromatograms obtained for synthetic mixtures on ordinary (*a*,*c*) and colloidal (*b*,*d*) SP having similar polarity factors; 120 °C; Solid carrier Celite-545: *a*) SE-30, *b*) PS–squalane (*c* = 0.2); *1*) propionaldehyde, 2) thiophene, 3) n-octane, 4) o-xylene, 5) n-octanol, 6) o-cresyl acetate; *c*) Reoplex-400, PS–PEG-400 (*c* = 0.5); *1*) n-pentane, 2) acetone, 3) chloroform, 4) toluene, 5) dioxan, 6) n-butanol, 7) isopentyl alcohol[20,21].

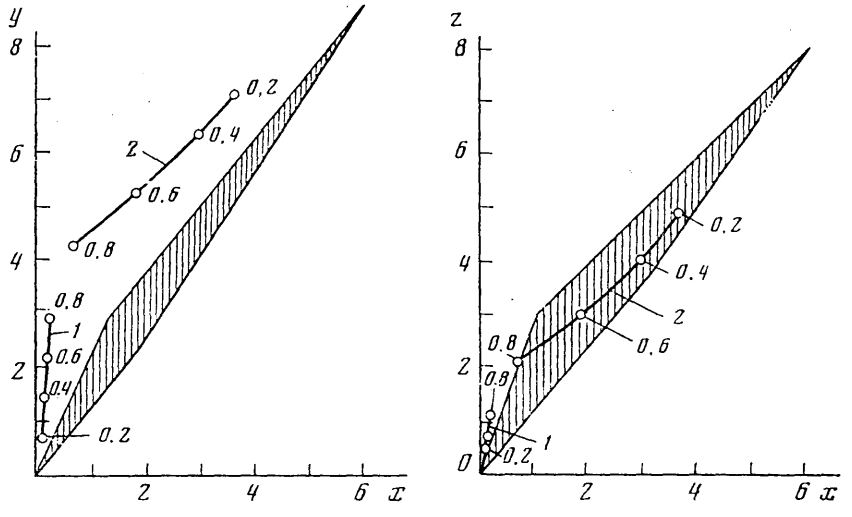


Figure 9. Dependence of the polarity factors y and *z* on the polarity factor *x*: *1*) PEG-400–Aerosil (*c* = 0.2, 0.4, 0.6, 0.8), 2) squalane–Aerosil (*c* = 0.2, 0.4, 0.6, 0.8) (the range of stationary phases studied by Rohrschneider[37] is hatched).[39]

The data in Table 3 can be used to select a sorbent with optimum selective properties on the basis of available materials produced by Soviet industry. The data given show that the use of colloidal stationary phases based on Aerosil and carbon black and a few modifiers makes it possible to obtain a set of sorbents covering a fairly wide range of polarity. Thus the polarity factor *y*, characterising the retention of ethanol, can be changed gradually from 0 on pure squalane to 6.96 on a PEG-400–Aerosil sorbent with *c* = 0.2 [1,2,3-tris(β-cyanoethoxy)propane], which has the highest polarity factors among known stationary phases (*y* = 8.71).

Knowing the Rohrschneider polarity factors, it is possible to replace one stationary phase by another with similar values of the polarity constants. Table 4 gives the values of the polarity factors of standard and colloidal stationary phases with similar selective properties[26]. The values of the polarity factors for the colloidal sorbents were obtained at 60 °C. The data on the separation on the standard stationary phases were taken from a monograph[38]. Thus without resorting to

the use of expensive SP difficult to obtain, it is possible to achieve a similar separation on a colloidal sorbent with a definite component ratio.

A similar comparison of standard stationary phases with the colloidal organic systems PS–PEG-400 and PS–squalane has been carried out[20]. As an example illustrating the possibility of replacing the stationary phases usually employed by colloidal phases, Fig.8 gives identical chromatograms for mixtures of compounds with different structures.

Graphs giving the relationship between the composition of a binary colloidal system and the polarity factor have been published[39] (Fig.9). The colloidal systems examined have higher polarity factors y than the usual stationary liquids studied by Rohrschneider[37]. Thus colloidal sorbents not only provide an alternative, but also may ensure an original combination of polarity factors.

IV. EFFICIENCY OF COLUMNS WITH COLLOIDAL SORBENTS

To estimate the efficiency of columns with solutions of polymers as stationary phases, and also to take account of various factors influencing the spreading of the zones of the components being separated, the following characteristics have been used[20,21]: the height equivalent to a theoretical plate (H) and the height equivalent to a theoretical plate with infinite increase in the retention time (H_∞):[6]

$$H_\infty = Lb/5.545 \qquad (11)$$

where L is the column length, and b is a constant from the equation relating the half-width of the peak and the retention time ($\tau_{0.5} = a + bt_R$). The set of values of H and H_∞ can characterise the efficiency of a chromatographic column for the separation of mixtures including weakly sorbed and strongly sorbed components, that is it can indicate the limiting possibilities provided by the stationary phase being studied.

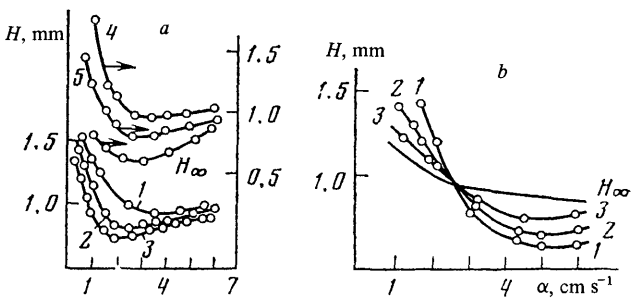


Figure 10. Relationship between the height equivalent to the theoretical plate and the linear velocity of the carrier gas at $\Pi = 15\%$ (*a*) and $\Pi = 3\%$ (*b*); PS–squalane ($c = 0.5$): *1*) hexane, *2*) heptane, *3*) nonane, *4*) benzene, *5*) toluene[20,21].

The regular features of the dependence of the efficiency of columns with colloidal stationary phases on the carrier-gas velocity, on the composition of the binary phase, and on the percentage impregnation of the carrier have been studied for a gel of polystyrene in squalane[20,21] (Fig.10). The nature of the change in the efficiency on going from one sorbent to another depends on the mechanism responsible for the broadening. The efficiency of columns with organic colloids in which the polymer is present in the liquid state is identical to that of columns with the pure modifier[20,21].

The efficiency of colloidal stationary phases based on highly dispersed adsorbents has been studied[26]. As noted above (see Fig.1), the sorptive capacities of the sorbents studied may differ considerably from one another, so that to estimate and compare their efficiencies it is appropriate to use the quantity $N = 5.545(t'_R/\tau_{0.5})^2$—the number of effective theoretical plates ($t'_R = t_R - t_0$ is the reduced retention time, and t_0 is the retention time of the non-sorbed gas). According to the data in Table 5, the efficiency of the stationary phase remains practically unchanged when a highly dispersed adsorbent is introduced into it, although in principle, a slight increase as a result of the decrease in the thickness of the liquid film should be expected[26]. Account must be taken, however, of the fact that the change to filled systems which have a higher viscosity than the pure modifiers leads to a decrease in efficiency. Thus in the final analysis, the values of N for a number of compounds are approximately the same on the individual liquid phase and on the liquid phase containing added adsorbents.

Table 5. Values of N for organic compounds on colloidal stationary phases[26].

Sorbate	PEG-400	PEG-400–Aerosil ($c = 0.2$)	PEG-400–carbon black ($c = 0.2$)
Nonane	680	670	660
Benzene	750	750	750
Methyl ethyl ketone	980	980	970
Ethanol	880	870	880
Nitromethane	690	700	690

The study of the dependence of the height equivalent to a theoretical plate on the carrier-gas velocity showed that, beginning from $V_a = 30$ cm^3 min^{-1}, the efficiency of a column with a colloidal sorbent depends little on the carrier-gas consumption for both organic and organometallic compounds[26]. Thus by using these sorbents it is possible to work in a fairly wide range of carrier-gas velocities without significant deterioration in the quality of the separation.

V. THERMAL STABILITY OF COLLOIDAL SORBENTS

One of the fundamental properties of a sorbent is its thermal stability. The limiting working temperature of sorbents can be determined in three ways: by recording the loss of liquid phase when the column is heated in a stream of carrier gas[40], by thermal analysis[41,42], and from the change in the background ion current with increase in the column temperature[43].

The most objective estimate of the thermal properties of chromatographic packing is given by thermal analysis, since in addition to the determination of the start of the mass loss from the form of the differential thermal curves, it is possible to deduce the nature of the processes responsible for the volatilisation of the stationary phase. The published thermal analysis curves[21] show that for colloidal polymeric phases, the temperatures of the start of mass losses and the start of the thermal effect generally coincide. This indicates that the changes in the mass of the colloidal stationary phases take place without significant thermal effects, and can be attributed to volatilisation.

Comparison of the upper temperature limits for colloidal stationary phases (Table 6) and the stationary phases usually employed in gas chromatography shows[19] that the thermal stability of the colloidal systems is equal to that of the individual modifiers and stationary liquids with similar polarity.

Table 6. Maximum working temperatures of colloidal phases, determined by extrapolation (medium—nitrogen, c' is the concentration of the vapour of the stationary phase in the carrier gas, g ml^{-1}).[21]

Stationary phase	$c'=10^{-6}$	$c'=10^{-7}$	$c'=10^{-8}$
PS–squalane (c = 0.9)	230	210	192
PS–PEG-400 (c = 0.8)	205	130	70
PS + 0.01% PEG-400	240	225	210

Although the addition of a polymer has no significant influence on the thermal characteristics of stationary phases, the addition of solid highly dispersed materials leads to an appreciable decrease in volatility. In the opinion of some authors[27,43], the effect is due to the binding of molecules of the liquid in the field of the adsorption forces of the active filler. For a high degree of dispersion and a sufficient quantity of highly dispersed material, all of the liquid phase is bound by adsorption, leading to a decrease in its volatility.

From the experimental data, it was concluded[27,43] that the stabilisation of stationary phases by Aerosil makes it possible to increase the maximum working temperature of the columns by 40–50 K, and makes it possible to increase the sensitivity of the chromatographic analysis using a flame ionisation detector by factors of 5–10, to increase the period of service of the columns, and to increase the accuracy of the treatment of the chromatograms by decreasing the distortion of the zero line.

Table 7. Values of K, $\bar{\Delta}$, and λ for colloidal and ordinary phases with similar polarity[20].

Mixture analysed	Stationary phase	t°, C	P	K	$\bar{\Delta}$	λ
1. Products of the catalytic dehydrogenation of butenes (acetone, acetic acid, acrylic acid, maleic anhydride)	25% PS in squalane (c = 0.4)	150	25	4.48	0.225	5.4
	25% Octoil-S	150	23	1.20	0.166	2.21
2. Products of the catalytic synthesis of isoprene (hexane, hexenes, hydropyrans, unsaturated alcohols, dimethyldioxan)	30% PS in dinonyl phthalate (c = 0.5)	100	26	1.00	0.182	3.64
	25% DNP	100	24	0.80	0.091	2.46
	15% PMPS-4	100	24	2.00	0.040	2;32
3. Aromatic hydrocarbons (benzene, toluene, cresyl acetates, naphthalene, ethylbenzene)	25% PS in squalane (c = 0.08)	150	10	2.10	0.059	3.10
	25% Apiezon L	150	9	3.48	0.040	2.32
4. C_2–C_{11} n-alcohols	25% PS in PEG-400 (c = 0.67)	180	58	1.10	0.085	0.91
	25 PEG-20000	180	64	1.43	0.032	0.71
5. C_1–C_6 aliphatic acids	25% PS in DNP (c = 0.2)	150	25	2.15	0.462	3.30
	DS-550 silicone oil	150	23	0.605	0.132	0.61
6. C_{10}–C_{24} n-alkanes	15% PS	250	62	1.00	0.704	2.08
	15% PEG-2000	250	64	1.10	1.157	1.60

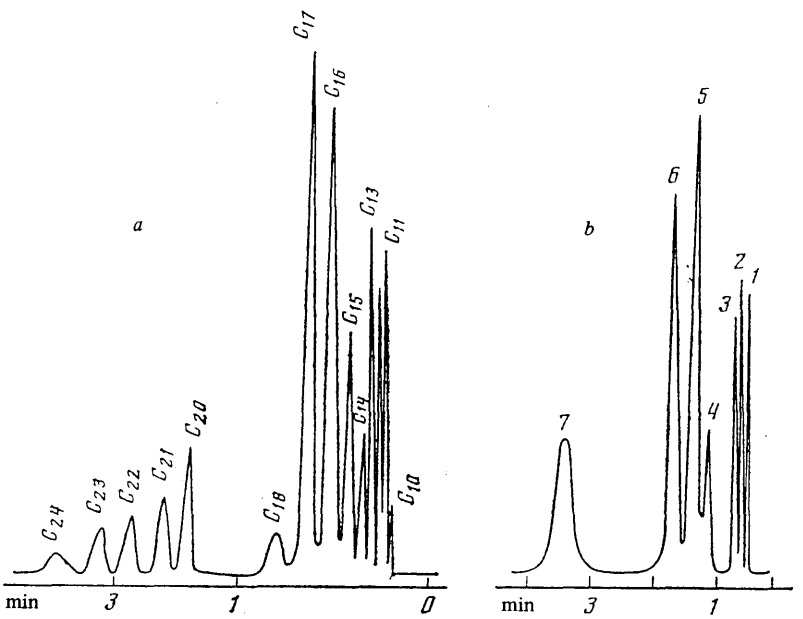


Figure 11. Chromatograms of mixtures of C_{10}–C_{24} n-alkanes (after the recording of the C_{18} peak, the diagram chart speed was decreased by a factor of 3) (*a*) and aromatic hydrocarbons and their derivatives (*b*): *1*) benzene, *2*) toluene, *3*) ethylbenzene, *4*) m-cresyl acetate, *5*) o-cresyl acetate, *6*) naphthalene, *7*) biphenyl[21].

A comparison of the thermographic curves obtained on a thermal analysis apparatus for PMS-100–Aerosil systems (c = 0.5) and for pure PMS-100, and also a study of the dependence of the mass losses by these sorbents on the time of passage of the carrier gas at 250 °C, showed that stationary phases stabilised by Aerosil have a higher thermal stability than the pure liquids[26].

VI. PRACTICAL APPLICATIONS OF CHROMATOGRAPHY IN A GAS–COLLOID SYSTEM

The universal character of colloidal stationary phases makes it possible to use them for the analysis of various organic and organometallic materials. As examples illustrating the possibilities provided by these sorbents, the conditions for the separation of various mixtures of direct practical interest are described below. In all cases, the colloidal stationary phases containing the highly dispersed adsorbents were deposited on silanised Chromaton. The solid carrier for the polymeric colloidal systems (except where otherwise indicated) was silanised Celite-545. In those cases where there is no reference to the source, the examples of the use of the sorbents developed were taken from Refs.21 and 26.

1. Analysis of Organic Compounds

Hydrocarbons. The low sorptive capacity of polymers makes it possible to use them to determine high-boiling substances at temperatures appreciably below the boiling points of the components being studied. Thus a mixture of C_{10}–C_{24} n-alkanes has been analysed on a column with polystyrene as stationary phase (Fig.11*a*) at 250 °C [b.p.(C_{24}) = 421 °C].[20] The response coefficient (Table 7) was greater by factors of ~6 and ~4 respectively than those on columns with Apiezon-L and polyphenylmethylsiloxane, usually employed in the analysis of n-alkanes. The time required for the analysis of the mixture of C_{10}–C_{24} n-alkanes was 5 min on the colloidal phase, and 30 min on Apiezon-L, for identical experimental conditions. A mixture of aromatic hydrocarbons and their derivatives was separated using a solution of polystyrene in squalane (c = 0.8) at 150 °C (Fig.11*b*).

Alcohols. The possibilities provided by the use of gas–liquid and gas–adsorption chromatography for the separation of high-boiling polar substances are limited by the low thermal stability of the polar liquid phases and the insufficient uniformity of the surface of most adsorbents, which leads to asymmetry of the peaks. The separation of C_2–C_{10} alcohols (boiling point of n-decanol 213 °C) on a column with the stationary phase PS–PEG-400 (c = 0.67) at 130 °C (Fig.12*a*) is therefore of interest.

Aliphatic acids. The analysis of free aliphatic acids (without conversion to the esters) on the usual stationary phases and diatomite carriers is extremely difficult, because of strong adsorption phenomena and the marked asymmetry of the peaks. Colloidal polymeric phases have been used for the direct separation of synthetic mixtures of C_1–C_6 aliphatic acids[20]. Fig.12*b* shows that the peaks of the acids are fairly symmetrical, and the analysis time is short (4 min). The conditions of the chromatographic separation were as follows: a 120 × 0.3 cm column was filled with a colloidal solution (15%) of polystyrene in dinonyl phthalate (c = 0.2) on silanised Chromosorb-W; 160 °C; nitrogen velocity 30 ml min^{-1}; specimen volume 0.025 μlitre.

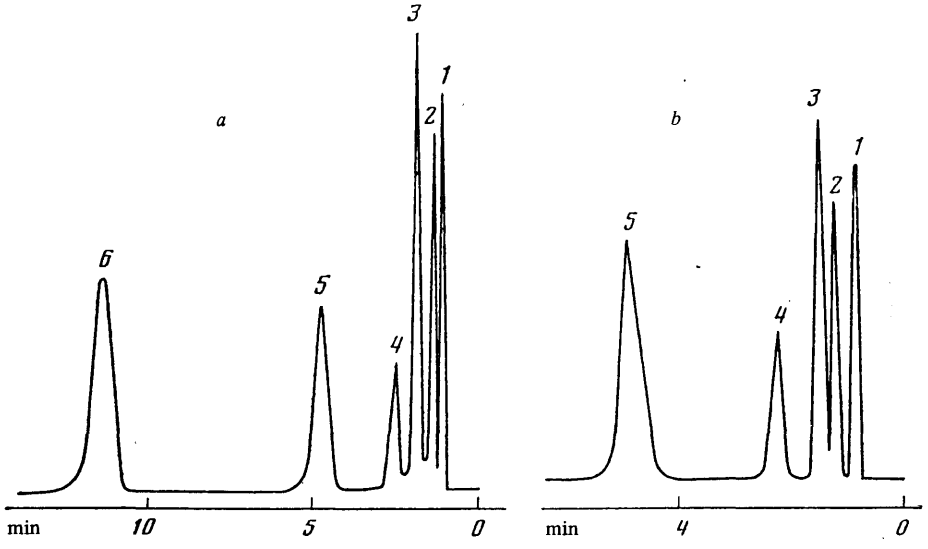


Figure 12. Chromatograms of mixtures of C_2–C_{10} n-alcohols (*a*): *1*) ethanol, *2*) propanol, *3*) butanol, *4*) pentanol, *5*) heptanol, *6*) decanol; and C_1–C_6 aliphatic acids (*b*): *1*) acetic, *2*) n-propionic, *3*) isobutyric, *4*) isovaleric, *5*) n-hexanoic.[21]

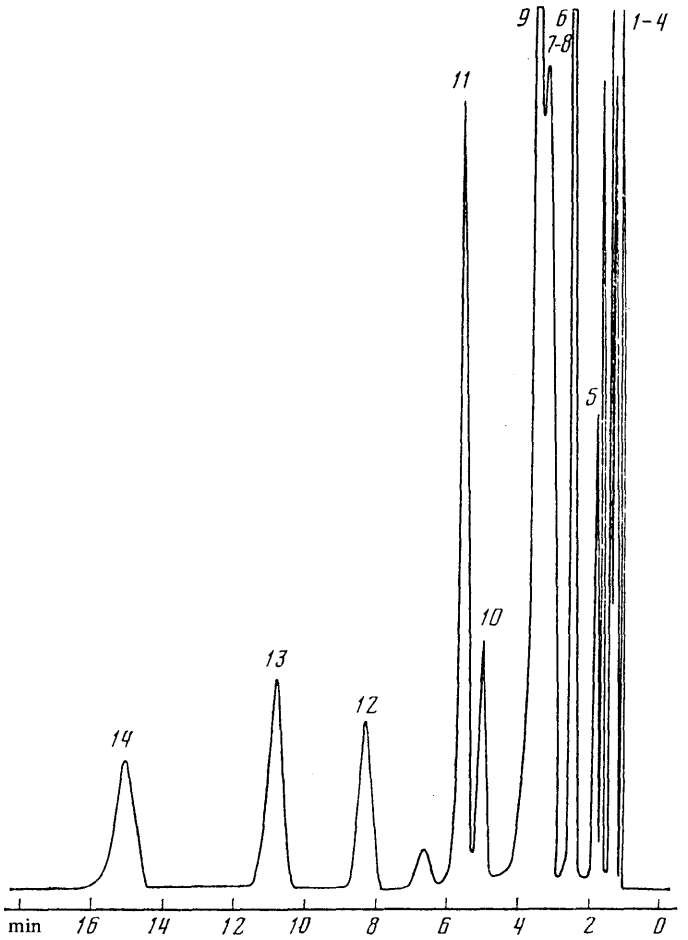


Figure 13. Chromatogram of petrol from the oxidative cracking of petroleum, boiling up to 100 °C: *1*) pentane, *2*) hexane, *3*) hexane, *4*) heptane, *5*) heptene, *6*) acetone, *7*) butyraldehyde, *8*) methyl ethyl ketone, *9*) benzene, *10*) ethanol, *11*) toluene, *12*) n-propanol, *13*) isobutyl alcohol, *14*) n-butanol[26].

Petrol from the oxidative cracking of petroleum. This petrol (fraction up to 100 °C), in addition to alkanes and aromatic hydrocarbons, contains oxygen compounds. It is difficult to separate this multicomponent mixture on an individual stationary phase. The largest number of peaks with a sufficiently regular distribution on the chromatogram was obtained using the colloidal system PEG-400–Aerosil (c = 0.5), deposited on a solid carrier in quantities of 20%. The chromatogram (Fig.13) shows that this sorbent makes it possible to separate the hydrocarbons from one another and from oxygen-containing compounds under isothermal conditions (column temperature 80 °C) on a column of length 2 m at a carrier-gas velocity of 40 ml min^{-1}. The colloidal sorbent had the following Rohrschneider characteristics: x = 2.37, y = 5.72, z = 3.51, and u = 6.12.

Products of the catalytic synthesis of acrylonitrile. The analysis of the highly dilute aqueous solutions is possible on a two-metre column using the stationary phase PS–PEG-400 (c = 0.67) at 100 °C and a carrier-gas velocity of 40 ml min^{-1} (Fig.14*a*).[20]

Mixture of moist air with hydrogen sulphide and ammonia. Symmetrical peaks for these substances (Fig.14*b*) are obtained using a colloidal solution of PS in PEG-400 (c = 0.3), deposited (in quantities of 30%) on Chromosorb-W (column length 2 m). The analysis is carried out initially at 50 °C, and after the ammonia peak has passed, the temperature of the thermostat is raised to 100 °C to achieve rapid elution of water.

Solution of t-butyl hydroperoxide and its decomposition products in chlorobenzene. Colloidal systems containing PM-15 carbon black have been used to analyse peroxides with a low thermal and catalytic stability[25]. t-Butyl hydroperoxide and its decomposition products have been separated[44] on a 120 × 0.4 cm column at 50 °C and a carrier-gas velocity of 70 ml min^{-1}, using dinonyl phthalate (30%) on Celite-545 as sorbent. By using a packing consisting of 20% of the system PEG-400–carbon black (c = 0.95) on the carrier, without changing the other parameters of the experiment, it was possible to decrease the time required for the analysis of the solution to 5 min (Fig.15*a*).

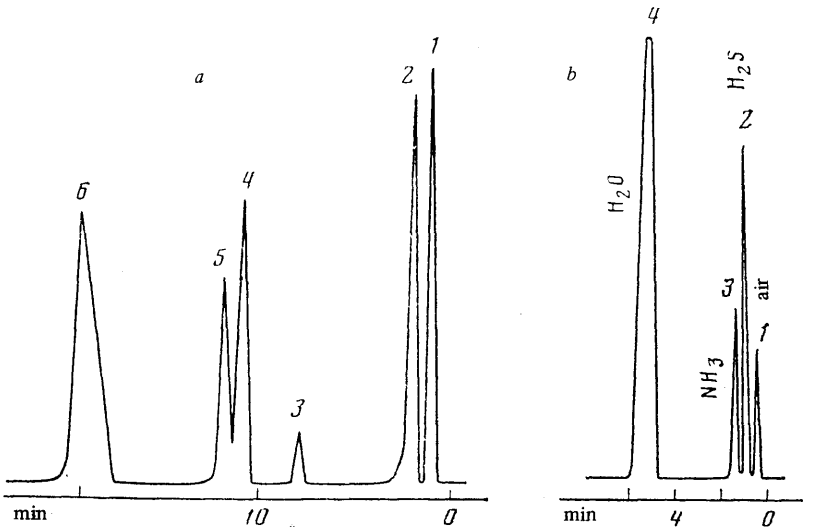


Figure 14. Chromatograms of mixtures of the products of the catalytic synthesis of acrylonitrile (AN) (*a*): *1*) air, *2*) ammonia, *3*) acrolein, *4*) AN, *5*) acetonitrile, *6*) water; and of moist air containing hydrogen sulphide and ammonia (*b*).[20,21]

Products of the catalytic dehydrogenation of butenes. The gas-chromatographic analysis of these products in the presence of large quantities of water has been carried out on a column of length 1.2 m containing a 25% colloidal solution of polystyrene in PEG-400 (c = 0.4) at 150 °C. On this sorbent, all the components were clearly separated, with completely symmetrical peaks (Fig.15*b*).

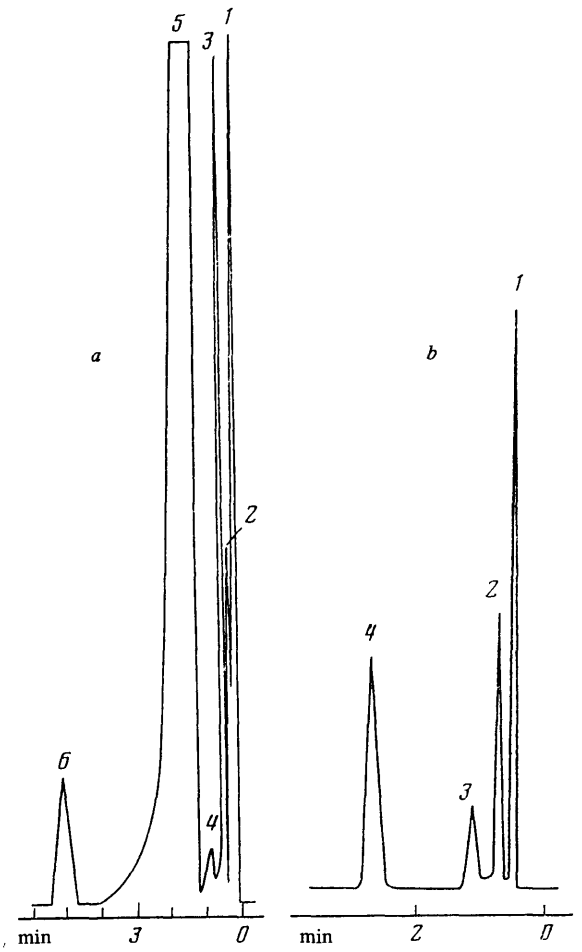


Figure 15. Chromatograms of mixtures of the products of the catalytic dehydrogenation of butenes (*a*): *1*) acetone, *2*) acetic acid, *3*) acrylic acid, *4*) maleic anhydride; and of a solution of t-butyl hydroperoxide and its decomposition products in chlorobenzene (*b*): *1*) acetone, *2*) methanol, *3*) t-butyl alcohol, *4*) di-t-butyl peroxide, *5*) chlorobenzene, *6*) t-butyl hydroperoxide[21,24].

Trace analysis. Conditions have been found for the gas-chromatographic determination of traces of biphenyl in diphenylamine, and of β-chloronaphthalene in naphthalene at 170 °C on the sorbent PEG-40000–Aerosil (c = 0.6).[26] The study of these solid solutions is of interest for the theory and practice of the production of semiconducting elements. Micro-analytical and spectral methods for the analysis of these systems are tedious and have a low sensitivity. The use of gas chromatography with colloidal sorbents has made it possible to lower the level of the quantitative determination of the impurity to 10^{-4}–10^{-5}% in the first case, and to 10^{-1} to 10^{-2}% in the second. The results of the determination of impurities in 1-ethyltricycloheptane-3-one[26] have been used to estimate the purity of the material for the precise study of its thermodynamic properties.

The results of the analysis of various synthetic mixtures and catalysates on ordinary and colloidal phases with similar polarity are given in Table 7. The following characteristics were used in the comparison of their selectivity: the degree of separation of the least effectively separated pair (K), the uniformity criterion ($\bar{\Delta}$), and the response coefficient (λ) [6]

$$\bar{\Delta} = n_c \tau K/t \qquad (12)$$

where n_c is the number of peaks, τ the width of the least broadened peak, and t the analysis time.

The response coefficient λ was calculated from the equation

$$\lambda = n_c K^2/t \ . \qquad (13)$$

Table 7 shows that the values of λ for the colloidal polymeric phases are higher than those for the ordinary phases. In the analysis of n-alcohols, PEG-20M gives a slightly better separation (K = 1.43) than the colloidal phase PS–PEG-400 (K = 1.10). If the decisive factor is the analysis time, however, it is necessary to compare the values of λ, and in this case the second phase is preferred.

Colloidal solutions of polymers have another significant advantage over the usual stationary phases: increase in temperature leads to a simultaneous increase in their selectivity and efficiency for the mixtures of substances examined, and this makes it possible to decrease the analysis time considerably without deterioration in the quality of the separation. Thus for example, the pair of substances most difficult to separate on the individual phase PEG-400 are not separated at all when the column temperature is increased from 100 °C to 120 °C, whereas under these conditions, the selectivity of columns with a colloidal stationary phase is increased by a factor of 1.1–1.4, leading to complete separation of the components being analysed[21].

2. Analysis of Organometallic Compounds

Most substances containing a metal–carbon bond are reactive and unstable to heat, and this makes it difficult to develop gas-chromatographic methods for determining organometallic compounds (OMC) and impurities in them. Thus in addition to the necessary resolving power, the chromatographic packing should have a low capacity, to ensure that the analysis can be carried out at low temperatures, and should be chemically inert with respect to the substances being analysed. These requirements are not satisfied by all liquid phases and adsorbents. Silicone stationary phases are fairly inert and hydrophobic, which is particularly important in work with readily hydrolysed compounds, and these phases have found extensive application in the gas-chromatographic analysis of OMC. Thus in a fairly complete review[45], more than 60% of all the examples of the analysis of OMC involved the use of stationary phases of the SE-30 and E-301 type. In the Soviet Union, the analogue of these SP with similar chromatographic polarity is the polymethylsiloxane liquid PMS-100.

The regular features of the chromatographic retention of alkanes and aromatic hydrocarbons by colloidal stationary phases based on PMS-100 and Aerosil have been studied[46]. It was shown that the addition of highly dispersed silica to the silicone stationary phase leads to a decrease in the specific retention volumes of heptane, benzene, biphenyl, and their derivatives. At the same time, the retention indices of aromatic compounds increase, and the selectivity of the

sorbent as a whole increases. Thus on going from the pure silicone to the sorbent with $c = 0.8$, the logarithmic retention index increases by 200 units for benzene, by 225 units for bibenzyl, and by 275 units for stilbene. Thus the possibility of achieving a smooth decrease in the sorptive capacity with an increase in the selectivity of chemically inert silicone SP by the dispersal of highly dispersed fillers in them facilitates the solution of the problem of separating and analysing OMC.

It is possible in principle to analyse a mixture of bis(arene) π-complexes of chromium (trade name Barkhos liquid) on silanised Chromaton with 6% of the colloidal system PMS-100–Aerosil ($c = 0.2$).[47] A clear-cut separation of organochromium compounds with boiling points of 315–340 °C was achieved on a 100 × 0.4 cm column at 185 °C (Fig.16). In earlier studies[48,49], Barkhos liquid was analysed at 200 °C and above. Even a slight decrease in temperature in the analysis of unstable compounds in order to decrease their decomposition in the column is theoretically and practically justified[50]. A decrease in the temperature of the experiment generally leads to an increase in the selectivity of separation. This makes it possible, by decreasing the length of the column, to reduce the analysis time, and this also leads to a decrease in the decomposition of the unstable specimen[51].

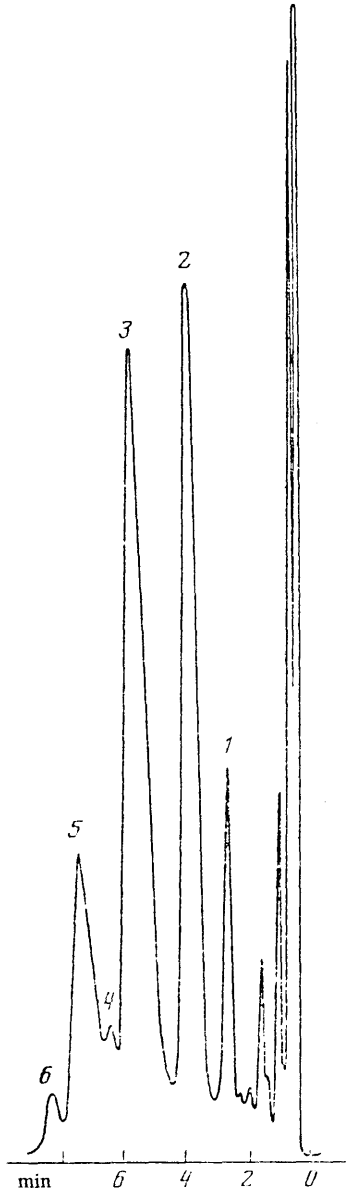


Figure 16. Chromatogram of a mixture of bis-arene π-complexes of chromium: *1*) benzene(ethylbenzene)chromium, *2*) bis(ethylbenzene)chromium, *3*) (ethylbenzene)(diethylbenzene)chromium, *4*) not identified, *5*) bis(diethylbenzene)chromium, *6*) not identified; SP—6% of the system PMS-100–Aerosil ($c = 0.2$); 100 × 0.4 cm column, 185 °C, carrier-gas velocity (hydrogen) 70 ml min^{-1}.[26]

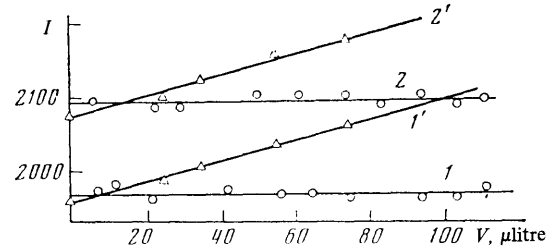


Figure 17. Dependence of the retention index on the quantity of organochromium liquid Barkhos added to the column: *1*, *2*) SP—6% of the system PMS-100–Aerosil ($c = 6$), 150 °C; *1'*, *2'*) SP—6% PMS-100, 200 °C; *1*, *1'*) bis(ethylbenzene)chromium, *2*, *2'*) (ethylbenzene)(diethylbenzene)chromium[53].

A subsequent study[52] of the dependence of the retention of the principal components of Barkhos liquid [bis(ethylbenzene)chromium and (ethylbenzene)(diethylbenzene)chromium] on the composition of the binary PMS-100–Aerosil system showed that the replacement of the silicone by the highly dispersed adsorbent, as in the case of hydrocarbons, leads to a decrease in the time required for the analysis of the organometallic compounds studied, and to an increase in the selectivity of their separation. On the basis of the observed regular features, it was suggested that the chromatographic analysis of Barkhos liquid be carried out on a column containing 6% of the colloidal system PMS-100–Aerosil ($c = 0.6$) at 150 °C, which lowered the temperature of the analysis by 35 K.[53] The usual method of lowering the temperature of the analysis by reducing saturation of the solid carrier with pure silicone does not work in this case because of the low selectivity of the lightly loaded column[53,54].

The advantage of carrying out the analysis at lower temperatures (by using a colloidal sorbent) is confirmed by the dependence of the retention indices of the OMC analysed on the number of specimens introduced into the chromatograph and expressed as the total quantity of Barkhos liquid passed through the column (volume of one specimen, 2 μlitre) (Fig.17). Fig.17 shows that on prolonged operation with a sorbent of 6% PMS-100 on Chromaton at 200 °C, there is a monotonic increase in the retention index, indicating the formation in the course of the analysis of a new stationary phase consisting of PMS-100 and the decomposition products of Barkhos liquid. This is also indicated by the almost complete change in the colour of the packing along the entire length of the column after the introduction of a total of 70 μlitre of the organochromium liquid. When 6% of the colloidal system PMS-100–Aerosil ($c = 0.6$) on the same carrier was used at 150 °C, however, the retention index and the colour of the sorbent along the entire length of the column remained practically unchanged during repeated analyses.

Colloidal SP based on Aerosil and PMS-100 have also been used to separate the organometallic compounds of the group VI elements[26,53,55]. The relative retention volumes and logarithmic retention indices have been determined[26] for arenetricarbonyl complexes of chromium (Table 8) and the hexacarbonyls of chromium, molybdenum, and tungsten at 50 °C on PMS-100–Aerosil (c = 0.4):

Compound	Chromium hexacarbonyl	Molybdenum hexacarbonyl	Tungsten hexacarbonyl
V^{rel}	1.00	2.03	4.14
I	746	826	903

Table 8. Chromatographic characteristics of the retention of chromium arenetricarbonyls (column temperature 170 °C).[53]

Compound	V^{rel}		I	
	SE-30 [56]	PMS-1000-aerosil (c = 0.4)	SE-30 [56]	PMS-100-aerosil (c = 0.4)
Benzenetricarbonylchromium	1.00	1.00	1595	1621
Toluenetricarbonylchromium	1.21	1.68	1604	1744
Mesitylenetricarbonylchromium	1.67	2.09	1722	1794
Anisoletricarbonylchromium	2.03	2.60	1805	1853
(Ethyl benzoate)tricarbonyl-chromium	2.58	3.24	1876	1906

The relative retention volumes and retention indices of all the arenetricarbonyls are greater on the column with the colloidal sorbent than on the column with SE-30. Thus in addition to dispersion interaction, the retention of the sorbates involves specific forces determined by the interaction of the carbonyl groups of the compounds studied with the Aerosil surface. The calculated retention indices can be used to identify metal carbonyls.

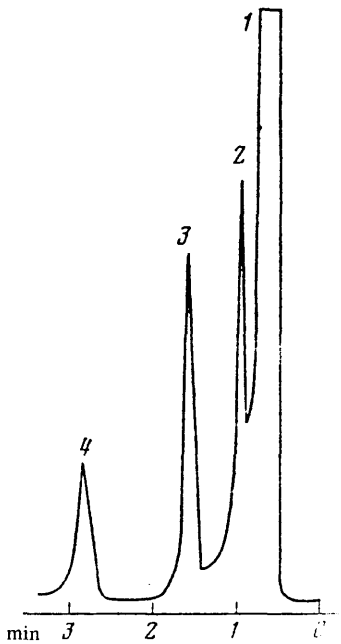


Figure 18. Chromatogram of the separation of group VI metal hexacarbonyls: *1*) chloroform, *2*) chromium hexacarbonyl, *3*) molybdenum hexacarbonyl, *4*) tungsten hexacarbonyl, SP—6% of the system PMS-100–Aerosil (c = 0.4), 200 × 0.3 cm column, 50 °C, carrier-gas velocity (hydrogen) 50 ml min^{-1}.[53]

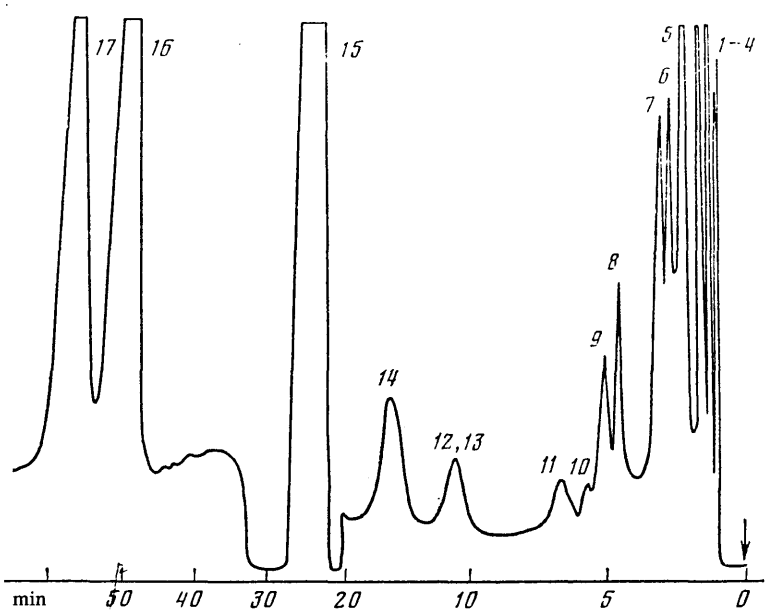


Figure 19. Chromatogram of impurities in tetraethyllead: *1*) ethane, *2*) butane, *3*) hexane, *4*) ethyl chloride, *5*) methylheptane, *6*) octane, *7*) octene, *8*) nonane, *9*) nonyne, *10*) nonadiene, *11*) benzene, *12*) ethanol, *13*) toluene, *14*) s-butyl alcohol, *15*) tetraethyllead, *16*) isobutyltriethyllead, *17*) n-butyltriethyllead, SP—20% of the system PEG-400–Aerosil (c = 0.3), 200 × 0.3 cm column, 70 °C, carrier-gas velocity (nitrogen) 20 ml min^{-1}, specimen volume 0.5 μlitre, instrument scale 10^{-11} A, recorder chart speed 600 mm h^{-1} for peaks *1–14*, 240 mm h^{-1} for peaks *15–17*.[58]

The use of the colloidal sorbent made it possible to separate the hexacarbonyls of chromium, molybdenum, and tungsten at 50 °C in 3 min (Fig.18).[53] In other studies[57], a similar mixture was separated at 90 °C in 7 min.

A stationary phase consisting of the binary system PEG-400–Aerosil (c = 0.3) has been proposed for the gas-chromatographic determination of impurities in tetraethyl-lead at the 10^{-4}–10^{-5} vol.% level[26,58,59]. It is possible to detect ~20 impurities of different chemical character (Fig.19). In the analysis, 90% of the principal component was directed past the flame ionisation detector, ensuring its stable operation.

These examples show that the gas-chromatographic analysis of organic and organometallic compounds can be carried out successfully using colloidal SP based on standard highly dispersed adsorbents or polymers. The possibility of controlling the sorptive properties, the high separating power, the symmetry of the peaks due to polar substances, the low retention times of high-boiling reactive compounds of low stability, the possibility of analysing impurities and micro-impurities, and their ready availability indicate the promising possibilities provided by the use of these colloidal sorbents in gas-chromatographic practice.

3. Colloidal Systems in Capillary Chromatography

Capillary chromatograms are being used increasingly in scientific-research and factory laboratories. They have a higher specific permeability than packed columns, and this makes it possible to carry out separations on long columns with a low pressure drop. Long column lengths combined with a high efficiency of separation ensure high separating power. Capillary chromatography is therefore being used to solve the most complex problems of separation in analytical chemistry[60–62]. Capillary columns, however, have a lower selectivity than packed columns. This can be seen from Eqn.(14), relating the selectivity of a column K_S [not to be confused with the selectivity of the stationary phase $k_S = (\Gamma_2 - \Gamma_1)(\Gamma_2 + \Gamma_1)$] with respect to two components being separated to the Henry coefficients Γ_1 and Γ_2 and the ratio of the volumes occupied by the gas and liquid phases in the column ($\varkappa$ and $\varkappa_1$ respectively):

$$K_s = 2\,\frac{(\Gamma_2\varkappa_1 + \varkappa) - (\Gamma_1\varkappa_1 + \varkappa)}{(\Gamma_2\varkappa_1 + \varkappa) + (\Gamma_1\varkappa_1 + \varkappa)} = 2\,\frac{\Gamma_2 - \Gamma_1}{\Gamma_2 + \Gamma_1 + 2\varkappa/\varkappa_1}\ . \qquad (14)$$

Packed columns usually have values of $\varkappa/\varkappa_1$ in the range 5–35, and capillary columns values in the range 50–15000. The latter are therefore less selective, and to achieve the same separation, the number of theoretical plates in them must be 10–100 times that for packed columns[60]. The change to adsorption–absorption sorbents obviously makes it possible to decrease $\varkappa/\varkappa_1$ and to bring the selectivity of capillary columns close to that of packed columns.

Since metallic capillary columns are gradually being displaced by glass columns, the interest in these sorbents is increasing to an even greater extent, since the effective use of glass columns is largely determined by their internal surface, which should ensure effective wetting of the glass capillary by the liquid phase. Special treatment makes it possible to increase both the wettability of the glass and its absorptive power. Various methods for producing intermediate coatings in capillary columns have been described[2,60–62]; analysis of these results shows that good operating characteristics can be obtained using columns with a layer of highly dispersed material, deposited on the wall of the capillary at the same time as the liquid phase. To avoid blocking of the capillary tubes when the suspension is introduced and to produce a uniform coating, the particle size of the solid filler cannot exceed 10^{-6} cm, that is it should be at the colloidal level.

Colloidal components as intermediate layers have been used and studied by Blumer[63,64] and Horning and co-workers[65–68]. Blumer[63,64] established that Aerosil treated with trimethylsilane (trade name Silanox-101) shows hydrophobic properties and forms stable suspensions in many solvents. Its dispersions in organic binding agents at a low concentration of the solid phase form thixotropic gels and adhere firmly to the surface of metal, glass, and polymers, making it possible to obtain a thin mechanically strong film of the stationary phase. Intermediate porous layers have been obtained by preparing a mixture of 0.2–0.5 g of the liquid phase (Apiezon-L, PEG-20M, FFAP, Emulphor, SE-30) in 10 ml of a solvent (methylene chloride, chloroform, or their mixtures with methanol) and 0.4–0.65 g of Silanox. Before the column was filled, the suspension was dispersed for 30 s in an ultrasonic bath. To predict qualitatively the efficiency of a column with this coating, a clean polished metal plate was wet with the prepared suspension. A smooth mechanically strong coating ensures good column operating conditions, whereas a dense granular surface with cracks and fractures after drying leads to a decrease in efficiency or to blocking of the capillary. To obtain thick porous layers, the suspension was introduced at a comparatively high rate (80 cm s^{-1}).[64] These columns have been used to separate mixtures of C_{16} to C_{18} methyl esters, normal alcohols, and homologues of benzene. For a specimen volume of 0.05 μlitre and HETT (height equivalent to a theoretical plate) = 1–1.3 mm, the separation time was several minutes.

Horning and co-workers[65,66], using intermediate layers with Silanox, obtained heat-resistant high-resolution glass columns suitable for the analysis of biological mixtures (steroids, acids, essential oils, and medicinal metabolites). Columns of length 60 m at 100–300 °C have given an efficiency of up to 100000 theoretical plates. A highly dispersed filler (6–10 μm), uniformly distributed in a surface film, prevented the formation of micro-droplets and breakdown of the stationary phase when the column was heated and cooled. The suspension was prepared by adding 2 g of Silanox to a solution of 0.5 g of SE-30 in 10 ml of CCl_4. To increase the sensitivity of the Silanox suspension, it was recommended that a solvent with a high density be used, or that a surface-active agent, for example benzyltriphenylphosphonium chloride, be added to the solution. The rate of passage of the suspension through the column was 5 cm s^{-1}. After drying for 3 h in a stream of nitrogen, the capillary column was covered with a basic layer of the stationary phase SE-30.

Glass capillary columns with heat-resistant polar phases have been described[67,68]. In the first stage, 20 m non-silanised borosilicate capillaries were wet with 1 ml of a suspension (0.1 g of the polar phase, 1 g of Silanox, and 100 ml of Silanox) (sic. Ed.of Translation), previously treated in an ultrasonic bath. The polar phase was then deposited on to the thin layer of suspension. A suspension of Silanox in a solution of the polymer of phenyl ether and phenyl sulphone (PZ-176) has been used to obtain a coating which makes it possible for a capillary column to operate at temperatures above 300 °C, and to separate the methyl esters of polyunsaturated aliphatic acids[75].

Longer columns (150 m) containing Silanox have been filled[69] by depositing intermediate coatings from a solution of 40 mg of the surface-active agent Igepol SO-880 in 10 ml of CCl_4 with the addition of 200 mg of Silanox. To increase the stability, the colloidal solution was placed for several minutes in a high-frequency furnace. The proposed method gives glass capillary columns with efficiencies of 437000–165000 theoretical plates. Their preparation is time-consuming, however (1 week).

A method for depositing colloidal intermediate layers to obtain polar capillary columns has been developed[70]. The stabilising additive was finely divided silica treated with benzyltriphenylphosphonium chloride (Cabosil), with particle size 15 nm and specific surface 190 $m^2 g^{-1}$. The suspension (0.3 g OV-225, 0.3 g silica, and 50 ml CCl_4) was treated in an ultrasonic bath and then passed through the column at a rate of 4–5 cm s^{-1}. An additional layer of OV-225 was deposited dynamically from a 10% solution in toluene. The thicknesses of the colloidal coating and the film of stationary phase, determined using the scanning electron microscope, were 0.3 μm and 0.4–1.2 μm respectively. The high stability of the film was attributed[70] to the porosity of the structure and the rheological properties of the intermediate layer. The proposed capillary columns have been used to separate mixtures of pesticides and steroid derivatives.

In the works cited, colloidal systems based on highly dispersed adsorbents were used as supports for the basic separating layer of stationary phase. The intermediate coating essentially increases the stability and capacity of the capillary column. The possible direct use of colloidal systems as stationary phases in capillary chromatography is also of interest, however.

Copper columns of length 25 m, containing as stationary phase a mixture of PEG-400 and Aerosil in the ratio 4 : 1, were recently described[28]. The suspensions were prepared in methanol solution. The separating characteristics of columns filled with pure PEG (column 1) and the colloidal stationary phase PEG-400–Aerosil (c = 0.2) (column 2) were compared. The quality of the columns was estimated from the number of theoretical plates N, the selectivity coefficient of the column K_S, and from the chromatograms of mixtures of organic compounds. Table 9 shows that, while giving almost the same efficiency, the columns containing the colloid are more selective in the separation of alcohols and hydrocarbons.

Table 9. Selectivity coefficients of the capillary columns 1 (N = 169000) and 2 (N = 162000).[28]

Substance	Column 1	Column 2
Methanol–ethanol	0.050	0.240
Ethanol–isopropyl alcohol	0.025	0.128
Ethanol–n-propanol	0.342	0.462
Decane–undecane	0.292	0.522
Benzene–decane	0.074	0.204

Thus the use of colloidal systems as intermediate stabilising layers and as stationary phases is extending considerably the possibilities provided by capillary chromatography, the most effective method of separating complex mixtures.

VII. FUTURE DEVELOPMENT OF CHROMATOGRAPHY IN A GAS–COLLOID SYSTEM

The analytical possibilities provided by chromatography in a gas–colloid system have not been exhausted. In the future, the extension of the range of application of colloidal sorbents already developed, and the production of new sorbents based on components which have not yet been studied chromatographically, can be expected. Some possible ranges of application and properties of colloidal stationary phases indicating their promising possibilities are described below.

The possibility of the extensive control of the selectivity, and the high thermal stability and availability of colloidal sorbents, can be used successfully to solve problems associated with the separation of multicomponent mixtures of substances belonging to different classes, in the analysis and trace concentrations, in analysis under programmed-temperature conditions, and in chromatographic–mass-spectrometric studies. The same properties, and the possibility of achieving a high capacity with a significant saving of stationary liquid phase, makes the use of colloidal sorbents promising in preparative chromatography. Colloidal stationary phases are used extensively in capillary chromatography, because of their high separating power and good operating characteristics. The possibility of lowering the temperature of the analysis by decreasing the capacity of the sorbent without a deterioration in the separating characteristics of the column, ensured by the use of colloidal systems, may be useful in the chromatographic analysis of compounds unstable to heat. The addition to the liquid phase of colloidal particles forming complexes with the compounds being analysed is promising in connection with the production of super-selective sorbents.

Among the important developments extending the possibilities provided by gas chromatography on colloidal sorbents is the use as fillers of higher dispersed adsorbents with chemically grafted organic groups, colloidal metals, and organometallic complexes, which make it possible to obtain heat-resistant sorbents with different selectivities. The development of analytical chromatography in a gas–colloid system will undoubtedly stimulate the use of gas chromatography as an effective method for studying colloidal systems. Reverse gas chromatography can be used to study sol–gel transitions, to determine the disjoining pressure and heats of displacement, to study adsorption at the boundary between a dispersed phase and the dispersion medium, etc. At the same time, the use of rheological methods and infrared and NMR spectroscopy will make possible a theoretically well-founded approach to the production and study of new colloidal sorbents for gas chromatography.

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Uranium Phosphates

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The methods of preparation, stability in solution and in the solid state, and composition of the crystalline hydrates of uranyl and uranium(IV) orthophosphates and condensed phosphates have been reviewed. The structures of these compounds have been discussed; they are three-dimensional polymers with a uranyl-phosphate framework.
The polymerisation of the phosphate anion on thermal decomposition has been discussed. Condensed uranyl polyphosphates are unstable when kept, and are capable of undergoing dehydration, the extent of which increases with increase in the length of the phosphate chain and increase in the uranium concentration.
The bibliography contains 199 references.

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I. INTRODUCTION

There is now a large amount of experimental and theoretical data on phosphates. The wide variety of these compounds is due to the high reactivity of the PO_4^{3-} group, and also the possibility of various combinations of phosphates. Phosphates have been the subject of a number of monographs[1-3] and reviews[4-6], in which the preparation, structural analysis, and spectral and thermal properties have been summarised. There are few publications, however, which systematise data on the phosphates of one element or several elements with similar properties, including orthophosphates and condensed phosphates (such as, for example, that devoted to the phosphates of quadrivalent metals[6]).

Extensive data on uranium phosphates have now accumulated, and require reviewing. The uranium compounds are mainly uranyl complexes containing the UO_2^{2+} group, of the oxo-group type MO_2^{2+} and MO^{2+}, which show a number of common structural and physicochemical properties.

In the present review, an attempt has been made to systematise available data on uranium phosphates. This has been done before, but the studies were incomplete. For example, in Ref.7, uranyl phosphates were examined from the viewpoint of the stability of their crystalline hydrates under isobaric conditions, and in Ref.8 the crystal chemistry of uranium minerals, including phosphorus-containing minerals, was discussed.

In the number of forms and variety of minerals, the class of uranyl phosphates is fairly representative[8]. Of 200 known minerals, it includes about 20 types, which can be divided into three crystal-chemical groups, on the basis of the $UO_2:PO_4$ ratio.

I. $UO_2:PO_4 = 1:1$ — autenite–meta-autenite or uranium phosphate micas.

II. $UO_2:PO_4 > 1$ — phosphuranylite.

III. $UO_2:PO_4 < 1$ — parsonsite.

The first group of minerals is made up of double uranyl phosphates with the alkali and alkaline earth metals, Cu, Mn,

Al, Fe, and hydrogen. The crystals of the minerals of the first group have a layer structure. The structure of meta-autenite $Ca[(UO_2)_2(PO_4)_2].6H_2O$ was studied in Ref.9, and later confirmed in Ref.10.

The second group includes minerals in which the ratio $UO_2:PO_4$ is most frequently 3:2 or 4:3. The crystal-chemical formulae of the minerals of this group have not been finally established, with the exception of dumontite $Ca(UO_2)_2(PO_4)_2.10H_2O$ and phosphuranylite $Pb(UO_2)_4(PO_4)_2(OH)_2.3H_2O$.[11] This group of minerals probably also includes the recently described phuralumite $Al_2(OH)_2(PO_4)_2(UO_2)_3(OH)_6.10H_2O$ and upalite $Al(UO_2)_3(PO_4)_2(OH)_3$,[12,13] whose structures are analogous to that of dumontite, and consist of $[(OH)_2(PO_4)_2.(UO_2)_3]_n$ layers. The crystal-chemical structures of the minerals of the parsonsite group have not yet been established.

Although considerable progress has been made in the crystal chemistry of uranium compounds, a number of problems relating to phosphorus-containing minerals have not yet been resolved. These include the question of the form in which uranium is present in the minerals, how to ensure the reliable determination of the $UO_2:PO_4$ ratio (errors in the determination of this ratio often lead to incorrect descriptions of chemical formulae), and how to systematise the nomenclature of the compounds. Since the study of minerals is often made difficult by such factors as the presence of impurities, the isomorphous replacement of elements, a low concentration of uranium, etc., the study of synthetic analogues of the natural compounds may help considerably in the determination of the degree of hydration and the form in which uranium is present in the compounds, and in establishing the regular features of the binding of the metal in different groups of atoms inside and outside the coordination sphere.

II. URANIUM ORTHOPHOSPHATES

1. Behaviour in Solution

The preparation of uranyl orthophosphates was the subject of lively discussion for a long time (until the nineteen-sixties). Some authors believed that the normal phosphate could not be isolated[14], and others that the dihydrogen phosphate could not be obtained[15]. The preparation of the compounds $P_2O_5.2UO_3.H_2O$, $P_2O_5.3UO_3$, and $P_2O_5.UO_3.2H_2O$, corresponding to the monohydrogen phosphate, the normal phosphate, and the dihydrogen phosphate, was reported[16]. It was noted that the composition of the precipitates is influenced by the $UO_3:P_2O_5$ ratio in the solution. The conditions of formation of uranium orthophosphate were studied most systematically by Schreyer and Baes[17,18], who examined the solubility of uranyl orthophosphates in phosphoric and perchloric acid solutions over a wide concentration range (0.001–15 M). They identified three stable phases at the following phosphoric acid concentrations:

$$[(UO_2)_3(PO_4)_2\cdot 6H_2O] < 0.014\,[PO_4^{3-}]\ M$$
$$[UO_2HPO_4\cdot 4H_2O] = (0.014 \div 6.1)\,[PO_4^{3-}]\ M$$
$$[UO_2(H_2PO_4)_2\cdot 3H_2O] > 6.1\,[PO_4^{3-}]\ M\ .$$

The dependence of the solubility of $UO_2HPO_4.4H_2O$ on the acid and salt concentrations was studied[18]. The existence in solution of the complexes $UO_2H_2PO_4^+$ and $UO_2H_3PO_4^{2+}$ was postulated.

Studies in solutions of constant ionic strength[19] confirmed the existence of the first complex, with formation constant 15.5, and also of $UO_2(H_2PO_4)_2$ and $UO_2(H_2PO_4)_2.H_3PO_4$ at PO_4^{3-} concentrations of ~ 1 M and 10 M respectively; their formation constants are 21.8 and 10.2 respectively. The solution of $UO_2HPO_4.4H_2O$ in perchloric acid (unlike that in phosphoric acid) is incongruent, depends on the surface area of the substance, and takes place via the formation of the sparingly soluble normal orthophosphate[20].

Pavkovic and co-workers[21,22] returned to the question of the formation and stability of orthophosphates in phosphoric acid solutions in a study of the precipitation and dissociation of complexes in aqueous solutions of phosphoric acid (2×10^{-6}–6 M) and uranyl nitrate (3×10^{6}–0.5 M). In an excess of the latter, the only product is the normal orthophosphate, which is present in equilibrium with solutions with a total PO_4^{3-} concentration of 3×10^{-3} M or less. Prolonged treatment of the normal orthophosphate (more than 24 d) converts it into the monohydrogen phosphate; the PO_4^{3-} concentration should be greater than 1.5×10^{-6} M. An important feature of this work[21,22] was the determination of the equilibrium conditions for the formation of the normal orthophosphate and the monohydrogen orthophosphate.

Comparison of the data of Refs.17 and 21 shows that they differ considerably at low and high phosphoric acid concentrations, and agree in the range 2×10^{-2}–2 M. The conversion of hydrogen phosphates into the normal phosphate is a common phenomenon, whereas the reverse process is comparatively rare. This characteristic feature of uranyl orthophosphates was noted by other workers[23], who converted the natural analogue trogerite $(UO_2)_3(PO_4)_2$ into the monohydrogen orthophosphate by keeping it in the equilibrium solution for six months. The normal phosphate is stable in air, whereas the monohydrogen phosphate is converted into the normal phosphate[16]. The compound $UO_2HPO_4.4H_2O$ is also stable when kept, and no changes were detected visually or by physicochemical methods in a specimen kept for 5 years. The best proof of its stability is the fact that it exists in nature as the mineral "hydrogen meta-autenite".

The synthesis from aqueous solutions of the so-called double uranyl phosphates containing other metal cations in addition to UO_2^{2+} is most complicated. A number of Soviet workers[24–26] have shown that normal and double phosphates may be formed under these conditions. The composition of the products depends on the concentration of the original solutions and the pH of the medium.

An attempt has been made to determine the relationship between the chemistry of the precipitation of the acidic, normal, and double orthophosphates[26,27]. A study of the conditions of precipitation of $NH_4UO_2PO_4$[26] showed that the reaction products may be normal ammonium orthophosphate and ammonium phosphatouranate, depending on the U:P ratio and the pH of the medium. A mechanism was proposed[26] for the formation of the phosphatouranate, including several stages. The uranyl ion is regarded primarily as the hydrolysed species $UO_2(OH)^+$,[28] so that formation of the normal orthophosphate is possible:

$$2UO_2(OH)^+ + UO_2^{2+} + 2HPO_4^{2-} + 4H_2O \rightarrow (UO_2)_3(PO_4)_2\cdot 6H_2O$$

$(UO_2)_3(PO_4)_2$ then reacts with the ammonium ion, giving a complex ammonium phosphatouranate

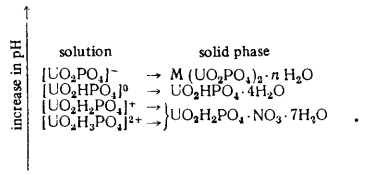
$$2(UO_2)_3(PO_4)_2\cdot 6H_2O + 2NH_4^+ \rightarrow (NH_4)_2(UO_2)_5(PO_4)_4\cdot 6H_2O + UO_2^{2+} + 6H_2O\ .$$

In an excess of ammonium phosphate, it is converted into $NH_4UO_2PO_4$:

$$(NH_4)_2(UO_2)_5(PO_4)_4\cdot 6H_2O + 3NH_4^+ + HPO_4^{2-} + 9H_2O \rightarrow 5NH_4UO_2PO_4\cdot 3H_2O\ .$$

It is believed[26] that the same reactions take place when uranyl salts are titrated with different phosphates (Na, K, Ca, etc.). It is suggested that the $(UO_2)_5(PO_4)_4^{2-}$ group is very stable, and forms part of a number of minerals. For a ratio U:P = 1:1, the following pH dependence of the stability

of the complexes was proposed:



Analysis of the data in Ref.26 reveals a number of discrepancies. First of all, it is not clear how the formation of ammonium phosphatouranate can be preceded by the formation of two compounds — $(UO_2)_3(PO_4)_2$, which is the least soluble uranyl orthophosphate (Table 1), and also a product containing the $(UO_2)_5(PO_4)_4^{2-}$ group, assumed[26] to be extremely stable—which are converted into ammonium phosphatouranate merely by titration. The statement[26] that $(UO_2)_5(PO_4)_4^{2-}$ is present in various minerals, in particular phosphuranylite, was not confirmed by later structural studies[11]. The dependence of the composition of the reaction products on the pH of the medium was also noted in Ref.29. Weigel and Hoffmann[7] regarded all double phosphates and hence minerals of uranium(VI) as salts of $HUO_2PO_4.4H_2O$ in which hydrogen is replaced by alkali and alkaline earth metals according to the schemes:

$$HUO_2PO_4 + M^+ \rightarrow MUO_2PO_4 + H^+$$
$$2HUO_2PO_4 + M^{2+} \rightarrow M(UO_2PO_4)_2 + 2H^+ \quad .$$

Table 1. Solubility products (SP) of uranyl orthophosphates.

Phosphate	SP	Refs.	Phosphate	SP	Refs.
UO_2HPO_4	$3{,}5 \cdot 10^{-12}$	[32]	$NH_4UO_2PO_4$	$4{,}36 \cdot 10^{-27}$	[33]
UO_2HPO_4	$2{,}14 \cdot 10^{-11}$	[33]	$NH_4UO_2PO_4$	$3{,}6 \cdot 10^{-26}$	[29]
UO_2HPO_4	$10^{-12{,}0 \pm 0{,}1}$	[30]	$(UO_2)_3(PO_4)_2$	$10^{-49{,}7 \pm 0{,}5}$	[30]
$LiUO_2PO_4$	$2{,}4 \cdot 10^{-26}$	[38]	$(UO_2)_3(PO_4)_2$	$8{,}2 \cdot 10^{-50}$	[34]
$NaUO_2PO_4$	$10^{-24{,}21 \pm 0{,}07}$	[30]	$(UO_2)_3(PO_4)_2$	$4{,}73 \cdot 10^{-47}$	[35]
$NaUO_2PO_4$	$6{,}4 \cdot 10^{-24}$	[38]	$Ca(UO_2PO_4)_2 \cdot 6H_2O$	$10^{-47{,}28 \pm 0{,}20}$	[31]
KUO_2PO_4	$10^{-25{,}5 \pm 0{,}1}$	[30]	$Sr(UO_2PO_4)_2 \cdot 7{,}5\ H_2O$	$10^{-48{,}30 \pm 0{,}15}$	[31]
KUO_2PO_4	$8 \cdot 10^{-24}$	[38]	$Ba(UO_2PO_4)_2 \cdot 6\ H_2O$	$10^{-49{,}62 \pm 0{,}15}$	[31]
KUO_2PO_4	$7{,}76 \cdot 10^{-2{,}}$	[33]	$Cu(UO_2PO_4)_2 \cdot 9\ H_2O$	$10^{-52{,}10 \pm 0{,}15}$	[31]
$RbUO_2PO_4$	$1 \cdot 10^{-27}$	[38]	$Zn(UO_2PO_4)_2 \cdot 7{,}8\ H_2O$	$10^{-46{,}77 \pm 0{,}35}$	[31]
$RbUO_2PO_4$	$10^{-25{,}72 \pm 0{,}15}$	[30]	$Co(UO_2PO_4)_2 \cdot 7\ H_2O$	$10^{-46{,}80 \pm 0{,}20}$	[31]
$CsUO_2PO_4$	$10^{-25{,}31 \pm 0{,}20}$	[30]	$Ni(UO_2PO_4)_2 \cdot 10\ H_2O$	$10^{-46{,}86 \pm 0{,}25}$	[31]

The difficulties of obtaining double uranyl phosphates were avoided[29] by treating powdered uranyl monohydrogen phosphate with 4 *N* solutions of the corresponding metal chlorides.

The conditions of preparation and solubility of uranyl orthophosphates have been studied by a number of authors[30–34,36–38]. Data on the solubility of uranyl orthophosphates are summarised in Table 1. The solubility of double uranyl phosphates with the alkali metals decreases in the order Na > Cs > K > Rb > NH_4, and that for bivalent metals in the order Zn ≅ Co ≅ Ni > Ca > Sr > Ba ≧ Cu.

2. Crystalline Hydrates of Uranyl Orthophosphates

In solubility studies, the composition of the crystalline hydrates is generally not discussed, and in the study of the physicochemical properties of solid specimens, the data obtained by different authors on the water concentration do not agree. Thus for the normal orthophosphate, the formation of $(UO_2)_3(PO_4)_2.6H_2O$,[17] and heptahydrate[16], and the trihydrate[24] has been reported. Methods for synthesising the hexa- and tetrahydrates have also been proposed[17,39]. For the monohydrogen orthophosphate, there is more agreement between different authors, who assign to it the composition $UO_2HPO_4.4H_2O$ (except for a report of the hydrate $UO_2HPO_4.2.5H_2O$[40]). The compositions of the crystalline hydrates of double uranyl phosphates differ considerably. The stability ranges of the crystalline hydrates with respect to isobaric thermal decomposition with a constant partial pressure of water vapour above the crystalline hydrates have been determined[7] (Table 2).

Table 2. Compositions of the crystalline hydrates of uranyl orthophosphates and the temperature range of their stability at a water vapour pressure of 92.5 ± 0.5 mmHg[7].

Original orthophosphate	Number of moles of water					
	6	4	3	2	1	0
$UO_2HPO_4 \cdot 4H_2O$	—	20—50	—	60—80	90—160	>170
$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	—	20—120	—	—	160—220	>300
$LiUO_2PO_4 \cdot 4H_2O$	—	20—70	80—120	120—170	—	>190
$NaUO_2PO_4 \cdot 3H_2O$	—	—	20—70	—	90—160	>170
$KUO_2PO_4 \cdot 3H_2O$	—	—	20—70	—	(0,5 H_2O; 80—150)	>100
$NH_4UO_2PO_4 \cdot 3H_2O$	—	—	20—80	—	(0,5 H_2O; 130—140)	>140
$Mg(UO_2PO_4)_2 \cdot 9H_2O$	100	110	—	120—170	180—200	>230
$Ca(UO_2PO_4)_2 \cdot 10H_2O$	—	110	—	140—200	—	>240
$Sr(UO_2PO_4)_2 \cdot 8H_2O$	75—105	—	—	110—190	—	>200
$Ba(UO_2PO_4)_2 \cdot 8H_2O$	~60—70	—	—	100—180	—	>200

The processes of thermal dehydration of uranyl orthophosphates, in spite of differences in the data reported by different authors, can be examined from the simplified viewpoint of the formation of intermediate hydrates and anhydrous salts, and differ only in the stepwise character of the removal of water and the temperature ranges. This is confirmed by data on the dehydration of the monohydrogen orthophosphate. It has been reported[16] that $UO_2HPO_4.2H_2O$ is formed when the tetrahydrate is heated, and is stable up to 110°; the anhydrous phosphate exists in the range 150—500°. In Ref.41, the loss of 3.5 moles of water was observed in the range 30—180°, and complete dehydration at 230—250°. In Ref.42, three moles of water were removed up to 60°, to give the monohydrate, stable in the range 60—120°. In Ref.40, it is claimed that all the water of crystallisation is lost at 170°. Finally, in Ref.43 it is reported that 2.5 moles of water are lost at 60—70°, and all the water of crystallisation at ~220°. Published data on the dehydration of the normal and double phosphates are equally contradictory[16,29,39,44].

3. Uranium(IV) Orthophosphates

The synthesis of uranium(IV) phosphates has been described in detail[6], and these compounds will be discussed only briefly.

Attempts to prepare uranium(IV) orthophosphates were reported in the early nineteen-hundreds. Colani[45] described orthophosphates to which he assigned the compositions $U(HPO_4)_2.5H_2O$, $U_3(PO_4)_4.UCl_4.HCl$, and $M_2U(PO_4)_2$ (M = Na, K). They were obtained by fusing UO_2 with metaphosphates or pyrophosphates in molten alkali metal chlorides.

The synthesis and solubility of the monohydrogen orthophosphate were later studied by Schreyer[46], who isolated the gelatinous compound $U(HPO_4)_2.4H_2O$. When the compound was kept in equilibrium with phosphoric acid, it was converted into the hexahydrate, and at an H_3PO_4 concentration greater than 9.8 M into $U(HPO_4)_2.H_3PO_4.H_2O$. Blumenthal[47] reported the preparation of the hydrates $U(HPO_4)_2.2H_2O$ and $U(HPO_4)_2.5H_2O$. Moskvin and co-workers[48] studied the solubility of $U(HPO_4)_2.4H_2O$ in phosphoric acid solution, and found that it passes through a maximum due to the formation of the undissociated form of $U(HPO_4)_2$. The stability constants of the complexes $U(HPO_4)^{2+}$, $U(HPO_4)_2$, $U(HPO_4)_3^{2-}$, and $U(HPO_4)_4^{4-}$ were determined; $\lg \beta = 12.0$, 22.0, 30.6, and 38.6 respectively.

The problem of the synthesis of the normal orthophosphate has not been resolved. It was noted above that in Ref.45 the normal phosphate could not be obtained by the reaction of solutions of UCl_4 and trisodium phosphate, whereas in Refs.49 and 50 it is stated that this compound is formed and is stable at 800°, and in Ref.51 it was found to be stable to 900–1200°. In Ref.39 it was shown that the normal orthophosphate does not exist at 600°, and the product, which has the same U:P ratio, is a mixture of the pyrophosphate and uranium dioxide.

Uranium orthophosphates with the general formula $MU_2(PO_4)_3$ (M = Na, K) are said to be obtained by the reaction of the uranium oxides UO_2 and UO_3 with zirconium pyrophosphate is molten sodium and sodium chlorides, and also by the reaction of the melts with uranium monohydrogen phosphate in an inert atmosphere according to the scheme[52]:

$$U(HPO_4)_2 + NaCl \xrightarrow{850°} NaU_2(PO_4)_3$$
$$U(HPO_4)_2 + KCl \xrightarrow{750°} KU_2(PO_4)_3 \quad .$$

4. Conditions of Preparation

In Ref.53, the phosphate $UO_2HPO_4.4H_2O$ was synthesised by the method of Schreyer and Baes[17], and had the composition given by this formula. The ranges of stability of its crystalline hydrated formed at room temperature were determined by keeping the specimens under equilibrium conditions at different saturated water vapour pressures. The tetrahydrate is stable down to pressures of 0.15 mmHg, the monohydrate exists at lower pressures, and the hydrates are interconvertible. The products with two and three water molecules are mixtures of the mono- and tetrahydrates. Thus the existence of the hydrate $UO_2HPO_4.2.5H_2O$[40] appears unlikely. A noteworthy feature of the interconversion of the crystalline hydrates is the rearrangement of the crystal structure, which involves the intermediate formation of an amorphous product which subsequently crystallises to give the new phase. This effect was detected by X-ray diffraction and thermal analysis, which showed the appearance of an exothermic effect on the DTA curve at 70° during the dehydration of the monohydrogen orthophosphate[53].

In Ref.54, the normal orthophosphate was obtained by various methods[17,24,39], including hydrothermal synthesis (Table 3). In the latter, an equimolar mixture of 0.1 M solutions of uranyl nitrates or stoichiometric quantities of UO_3 and 0.1 M H_3PO_4[54] were placed in ampoules, sealed, and kept at 150° for 3–4 d. The X-ray diffraction patterns of the products obtained under hydrothermal conditions and by hydrolysis of uranyl monohydrogen orthophosphate coincide, but do not agree with the data of Ref.55. The reaction of uranyl nitrate with Na_2HPO_4[24] gave a precipitate with the composition $NaUO_2PO_4.3H_2O$ (Table 3). Dilute (0.01 M) solutions of uranyl nitrate and phosphoric acid give the amorphous normal orthophosphate, which binds ~ 6 moles of water; it is stable in air, but in a dry atmosphere it gradually loses water to give the tetrahydrate. Crystalline $(UO_2)_3(PO_4)_2.4H_2O$ is stable at room temperature at different water vapour pressures in the range 0–12 mmHg.

Table 3. Compositions of uranyl orthophosphates obtained by different methods.

No.	Synthesis conditions	Concentration of the components in the solid phase, %				Composition
		U	P_2O_5	Na	H_2O	
1	0.001 M $UO_2(NO_3)_2$ and H_3PO_4; 25 °C (Ref.17)	63.4	13.2	—	9.7	$(UO_2)_3(PO_4)_2 \cdot 6H_2O$
2	Ditto (Ref.17)	62.4	12.5	—	6.9	$(UO_2)_3(PO_4)_2 \cdot 6,3H_2O$
3	Hydrothermal synthesis, 0.1 M $UO_2(NO_3)_2$ and H_3PO_4; 150 °C, 72 h (Ref.54)	66.8	13.4	—	6.9	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$
4	Hydrothermal synthesis, 0.1 M UO_3 and H_3PO_4 (U:P = 3:2); 150 °C, 72 h (Ref.54)	65.9	13.6	—	6.5	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$
5	Hydrolysis of $UO_2HPO_4.4H_2O$ by water; 100 °C, 2 h (Ref.39)	67.1	13.7	—	6.8	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$
6	0.001 M $UO_2(NO_3)_2$ and 0.015 M Na_2HPO_4; 25 °C (Ref.24)	53.4	15.6	4.0	12.5	$NaUO_2PO_4 \cdot 3H_2O$
7	0.01 M $UO_2(NO_3)_2$ and 0.15 M Na_2HPO_4; 25 °C (ref.24)	52.9	16.3	4.2	12.9	$NaUO_2PO_4 \cdot 3H_2O$
8	Hydrolysis of $NH_4UO_2PO_4.3H_2O$ by boiling with 0.8 M HNO_3 (Ref.17)	54.2	16.9	—	12.3	$NH_4UO_2PO_4 \cdot 3H_2O$

To obtain double uranyl phosphates, it is necessary to maintain strictly definite pH values in the solutions. Thus ammonium uranyl phosphate $NH_4UO_2PO_4.3H_2O$ can be obtained only at pH 4.6–4.8 from solutions of uranyl acetate and diammonium hydrogen phosphate[56]. In Ref.57 it was found that in the NH_3–UO_2–H_3PO_4–H_2O system there exist two uranyl phosphates, containing 3.8% and 8.8% NH_3 respectively.

The compound $U(HPO_4)_2.4H_2O$ obtained by the method of Ref.48 is a gelatinous product which does not crystallise on prolonged standing (20–30 d) in the equilibrium solutions at room temperature and higher temperatures[58]. To improve the mechanical properties of the product, it was salted-out with organic solvents. Best results were obtained using isopropyl alcohol in the ratio reduced solution:alcohol ≅ 1:4.[58] Although the precipitate obtained was amorphous towards X-rays, it was readily filtered, washed, and dried. Hydrates containing more or less than $4H_2O$ of crystallisation could not be obtained by the methods of Refs.46 and 47. Hydrates with 2.5 and 1.5 moles of water are obtained by keeping $U(HPO_4)_2.4H_2O$ under equilibrium conditions at different saturated H_2O vapour pressures. The tetrahydrate is stable down to p_{H_2O} = 5 mmHg, $U(HPO_4)_2.2.5H_2O$ is stable in the range 4–2 mmHg, and $U(HPO_4)_2.1.5H_2O$ is stable at lower water vapour pressures.

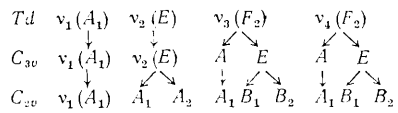
To resolve the question of the possibility of obtaining the normal orthophosphate[58], the conditions of its synthesis according to Ref.49 from solutions of UCl_4 and trisodium phosphate with subsequent heating of the precipitates to 600° were reproduced. At pH > 6, the precipitate is uranium hydroxide, and in acidic solutions, either the monohydrogen phosphate or chloride phosphates containing 58.6% U, 20.1% P_2O_5, 6.1% Cl, and 8.4% H_2O are formed; when the latter were heated at 600°, the product had a composition close to that of $U_3(HPO_4)_4$ (64.3% U, 23.6% P_2O_5), but consisted of a

mixture of the ortho- and pyrophosphates and uranium dioxide. The normal phosphate could not be obtained by the prolonged hydrolysis of $U(HPO_4)_2.4H_2O$ (20 d) at high temperatures. Thus the normal orthophosphate cannot be obtained, and products with a similar composition have been erroneously assumed to be normal uranium(IV) phosphate.

5. Physicochemical Properties

Until comparatively recently, there were few published papers on this topic[31,40,59,60]. A simplified interpretation of the bands in the infrared spectrum, involving their assignment to various vibrations of the uranyl ion and its overtones and combination tones, was carried out in Ref.59. The other papers do not give a detailed assignment of the bands of all the groups in the compound, and do not discuss the wavenumbers of the water vibrations, which make a significant contribution to the spectra of uranium complexes.

The characteristic ranges of absorption by each of the groups in uranyl orthophosphates are well known[3,61-63]. The free orthophosphate ion has a tetrahedral configuration, and has four fundamental vibrations with wavenumbers $\nu_1(A_1)$ ~ 940 cm^{-1}, $\nu_2(E)$ ~ 420 cm^{-1}, $\nu_3(F_2)$ ~ 1020 cm^{-1}, and $\nu_4(F_2)$ ~ 560 cm^{-1}, of which the two triply degenerate vibrations are infrared active[3,62]. On coordination to a metal, the symmetry of the PO_4^{3-} ion may be lowered from T_d to C_{3v} or C_{2v}, accompanied by the following changes in the spectral characteristics:



The infrared spectrum of $UO_2HPO_4.4H_2O$ in the range of the $\nu_3(F_2)$ vibrations shows two strong bands with maxima at 990 cm^{-1} and 1105 cm^{-1}; the $\nu_4(F_2)$ band is also split into two components. Thus the symmetry of the distorted phosphate tetrahedron is close to C_{3v}[64,65] (Table 4).

The ν(OH) stretching region contains a strong broad band with a maximum at about 3300 cm^{-1}, which merges with the band at 2200 cm^{-1}, and the $\delta(H_2O)$ region contains two bands, at 1640 cm^{-1} and 1750 cm^{-1}. From the broad bands of medium strength at 1750 cm^{-1} and 2200 cm^{-1}, it was first assumed that part of the water in the compound is present as hydroxonium ions H_3O^+,[66-68], formed by the transfer of protons from HPO_4^{2-} to H_2O. Evidence in support of this assumption was provided by the absence of δ(POH) absorption at 1200 cm^{-1} and 2400 cm^{-1}.[62,69]

A study of the ^1H NMR spectra of $UO_2HPO_4.4H_2O$,[70] however, showed the absence of the bands of width 10–15 G and 20 G characteristic of water of crystallisation and hydroxonium ions respectively[71-74]. Instead, the spectrum shows one narrow band of width only 0.1 G, which with decrease in temperature becomes broader, while retaining its singlet structure. This narrow line corresponds to weakly bound water molecules and protons with a high diffusion mobility, indicating that the proton is hydrated by water molecules to give the oxonium group $H_9O_4^+$. The criterion used to distinguish H_3O^+ and more complex oxonium groups was the absence of the totally symmetric deformations of H_3O^+ in the Raman spectra in the region of ~ 1200 cm^{-1}.[75] The extremely high mobility of the proton and water molecules in $UO_2HPO_4.4H_2O$ is indicated by the ease of deuteriation of the compound[70]. Treatment of a specimen in an atmosphere of D_2O vapour for 24 h is sufficient for complete isotopic replacement.

Thus the monohydrogen orthophosphate has a polymeric structure containing uranyl phosphate layers; water occupies the space between the layers, through which the mobile proton moves freely.

Table 4. Vibrational wavenumbers (cm^{-1}) of U^{VI} and U^{IV} monohydrogen orthophosphates*[64].

$UO_2HPO_4.4H_2O$	$UO_2HPO_4.H_2O$	$U(HPO_4)_2.4H_2O$	Assignment
254	250	—	$\nu_2(UO_2^{2+})$
290	287	—	$\nu(U-OPO_3)$
460	—	415	$\nu_2(HPO_4^{2-})$
544; 623	500; 533; 621	540; 610; 625	$\nu_4(HPO_4^{2-})$
825 (844)	850 (867)	—	$\nu_1(UO_2^{2+})$
923	926	—	$\nu_3(UO_2^{2+})$
—	990	920	$\nu_1(HPO_4^{2-})$
990 (990); 1105	1055; 1120	980; 1060; 1150	$\nu_3(HPO_4^{2-})$
—	1235	1265	δ(POH)
1640	1618	1625; 1700	$\delta(H_2O)$
1750; 2200	—	—	$H_9O_4^+$
—	2384±20	2400	ν(POH)
3300±20	3500±10	3200; 3400	ν(OH)

* The wavenumbers found in the Raman spectra are given in brackets.

On going to $UO_2HPO_4.H_2O$ there is an increase in the complexity of the infrared and Raman spectra; in the infrared spectra, the $\nu_3(F_2)$ band, as before, is split into two components (1055 cm^{-1} and 1120 cm^{-1}), which are displaced to larger wavenumbers by 65 cm^{-1} and 15 cm^{-1}. At the same time, the splitting $\Delta\nu_3$ decreases to 65 cm^{-1}. The $\nu_1(A_1)$ vibration is activated (990 cm^{-1}), and an additional $\nu_4(F_2)$ band appears at 500 cm^{-1}. An interesting feature is that the spectrum of the monohydrate contains bands at 1235 cm^{-1} and 2380 cm^{-1}, characteristic of the POH stretches and deformations of hydrogen orthophosphates. The ^1H NMR spectrum of $UO_2HPO_4.H_2O$ has the form typical of acid salts containing water of crystallisation and the proton of a hydrogen phosphate group. The molecules of water of crystallisation give a doublet of width 13.1 G. The calculated values of the second moment[76] and the distance between the protons[77] are 17.7 G^2 and 1.65 Å, typical of molecules of water of crystallisation. The central narrow component of width 1.3 G has a second moment of 2.2 G^2.

Thus the change from the tetra- to the monohydrate of uranyl monohydrogen orthophosphate leads to fixation of the mobile proton of the phosphate group and the formation of the acid salt, accompanied by a rearrangement of the structure[53].

Up to the present, relatively few solid compounds containing oxonium groups were known. Species of this kind with the general formula $H_{2n+1}O_n^+$ are extremely characteristic of solutions of strong acids[75,78-80]. In recent years, the improvement of physicochemical methods of study has made it possible to detect the dioxonium ion $H_5O_2^+$ in the hydrates of a number of complex acids: $H_3PWO_4.6H_2O$[81] and $H_2PtCl_6.nH_2O$[82]; $H_9O_4^+$ has been detected in $H_9O_4CF_3SO_3^+$[83] and $H_9O_4Cl.2H_2O$.[84]

The existence of the $H_3O_4^+$ group in uranyl monohydrogen orthophosphate distinguishes it from the series of acid phosphates with a fixed proton, and is responsible for its electrical conductivity. The presence of a proton gas, capable of moving along a line of hydrogen bonds, has been detected in studies of the electrical conductivity of various substances[85-90]. The conductivity, which is due to the migration of protons in the lattice, increases with increase in temperature. In fact, the electrical conductivity of a compressed disc of $UO_2HPO_4.4H_2O$ at a constant stabilised voltage of 3–6 V[70] begins to increase sharply at 72° by a factor of almost 10^6 compared with the original value (10^{-6} Ω^{-1} cm^{-1}), reaching a maximum of 0.2 Ω^{-1} cm^{-1} at 90°, after which it decreases equally sharply. A high proton conductivity in this phosphate was detected similarly by another group of workers[91] in the temperature range 20–60°. The anionic and electronic conductivity is negligibly small. The same authors[92] report that at 100 °C the proton conductivity of $UO_2HPO_4.4H_2O$ was 7×10^{-2} Ω^{-1} cm^{-1}, whereas the electronic conductivity is ~ 10^{-8} Ω^{-1} cm^{-1}. They discuss[92] the possibility of applying this phosphate in electrochemical devices, making use of such properties of the compound as the low solubility, corrosion resistance, ease of mechanical treatment, and ability to operate in the range 0–100°. According to their estimates[92], a cell having electrodes of CaH_2 and $TiFeH_2$ with uranyl monohydrogen phosphate as electrolyte will have an e.m.f. of 0.8 V and a theoretical specific energy of 294 W h kg^{-1}. The same authors[93,94] found by NMR that this compound in the temperature range 0–30° undergoes a phase transformation due to ordering of the hydrogen bonds in the structure; the diffusion of hydrogen at 20–70° has also been detected[95].

Comparison of data obtained by the present authors[53,64,70] with the data of Refs. 91–95 shows that the quantitative values of the electrical conductivity, the temperature range, and the explanation of the conductivity in terms of the migration of extremely mobile protons and water molecules for the most part agree; the views on the structure of the compound also coincide. The suggestion of the present authors that the substance has a layer structure involving a uranyl phosphate framework $(UO_2PO_4)_n^{n-}$ was confirmed by a calculation[96,97] for a fragment of the layer $[(UO_2)_nPO_4]^{5+}$ of symmetry D_{2d}, in which the heavy uranium atoms are practically at rest, and the kinematic interactions are weakly transmitted through them. The calculated vibrational wavenumbers show fairly good agreement with the experimental values for uranyl monohydrogen orthophosphate and double uranyl orthophosphates, and indicate that the calculation for the fragment of the layer model gives a sufficiently good qualitative description of the characteristic features of its structure. The conclusions about the structure of uranyl monohydrogen orthophosphate and double uranyl orthophosphates were confirmed by crystallographic data for $NH_4UO_2PO_4.3H_2O$,[98] the monohydrogen orthophosphate[99,100], and copper dioxophosphatouranate[101]. The structure of $UO_2HPO_4.4H_2O$ is made up of layers, containing UO_2^{2+} and PO_4^{3-} ions, and alternating two-dimensional networks containing water molecules. The U–O(PO_4) distance is 2.307 Å. In this compound there is a system of strong hydrogen bonds with O...O distances of 2.56–2.81 Å, which ensures proton migration and hence the electrical conductivity of the substance. When the proton is replaced by a metal or ammonium ion, the proton conductivity decreases sharply. The same result is achieved by removing part of the water, as for example in the monohydrogen orthophosphate monohydrate.

The structures of uranyl dihydrogen orthophosphate, normal uranyl orthophosphate, and uranium(IV) phosphates have not yet been determined. The spectra of these compounds have been analysed to determine their structural characteristics. On going from $UO_2(H_2PO_4)_2.3H_2O$ to $UO_2(H_2PO_4)_2.H_2O$ (the latter is stable at a water vapour pressure of 0.1 mmHg), the strength of the uranium–oxygen bond in the uranyl group increases (the ν_1 and ν_2 wavenumbers increase[102]). All the bands assigned to the $H_2PO_4^-$ vibrations are doublets (Table 5). It is suggested that the doublet structure of the bands is due to the existence of non-equivalent phosphate groups (see Table 5). A possible reason for the non-equivalence of the phosphate groups may be a difference in the influence of the hydrogen bonds of the water molecules on each $H_2PO_4^-$ group. In the monohydrate, where the influence of the water molecules is weaker, the splitting of the $H_2PO_4^-$ lines disappears.

Table 5. Vibrational wavenumbers (cm^{-1}) in the infrared spectra of hydrated uranyl dihydrogen orthophosphate*.

$UO_2(H_2PO_4)_2.3H_2O$	$UO_2(D_2PO_4)_2.3D_2O$	$UO_2(H_2PO_4)_2.H_2O$	$UO_2(D_2PO_4)_2.D_2O$	Assignment (Ref.102)
259	260	260	260	ν_2 (UO_2^{2+})
351 (365); 391 (400); 492; 536	346; 388; 503; 543	369; 430 (445); 505;	370; 423; 508	δ (PO_2)
561; 631; 765	425; 465; 555	559; 672; 753	558	ω (H_2O, D_2O)
836 (835)	836	(860)	—	ν_1 (UO_2^{2+})
900 (912)	900	900 (920)	900	ν_s (PO(H))
921	924	933	933	ν_s (UO_2^{2+})
973; 991	974; 999	999	999	ν_{as} (PO(H))
1084 (1064)	1074	1064 (1058)	1070	ν_s (PO_2)
1109	1103	—	—	ν_{as} (PO_2)
1131 (1130)	1127	—	—	ν_s (PO_2)
1183	1175	1163	1159	ν_{as} (PO_2)
1220; 1280	825; 860	—	820	δ(POH, POD)
1600; 1627	1147	1588	1143	δ (H_2O, D_2O)
2400	1800	—	—	ν (OH, O—H... O)
2700; 3000	2100; 2247	3137	2250	ν (PO—H, PO—D)
3200; 3360; 3530; 3572	2352; 2576; 2621; 2660	2522; 3577	2573; 2612; 2656	ν (OH, OD)

* The wavenumbers found in the Raman spectra are given in brackets.

The existence in $UO_2(H_2PO_4)_3.3H_2O$ of a system of strong hydrogen bonds and the participation of the phosphate anion in this system are indicated by the absorption in the ν(OH) region from 3600 cm^{-1} to 2600 cm^{-1}, the band of medium strength at 2550–2100 cm^{-1}, and the broad bands in the P–OH deformational region (1300–1100 cm^{-1}). The protons of the $H_2PO_4^-$ groups apparently form H-bonds with water molecules, giving bridged O...O structures[102-106]. Comparison of the spectra of dihydrogen orthophosphate specimens hydrated to different extents gives information on the state of the water in the compounds. The splitting of the $\delta(H_2O)$ band into two components at 1600 cm^{-1} and 1627 cm^{-1} in the spectrum of $UO_2(H_2PO_4)_2.3H_2O$, which increases with decrease in temperature, indicates that the water molecules in this compound are structurally non-equivalent. The spectrum of the monohydrate shows only one band at 1588 cm^{-1}, and the ν(OH) and δ(POH) bands tend to be narrower. At the same time, the broad range of absorption with a maximum at 2400 cm^{-1} disappears, and the two ν(OH) bands at 3572 cm^{-1} and 3530 cm^{-1} are preserved. The high values of ν(OH) and the low value of $\delta(H_2O)$ indicate that there is little distortion of the water molecule in the monohydrate under the influence of hydrogen bonds. At the same time, the difficulty of

removing the last H_2O molecule indicates that it is strongly bound in the structure, which is possible if it is coordinated to uranium. The infrared spectrum (Fig.1) shows bands due to the librational vibrations of water, which are sensitive to deuteriation and to decrease in temperature[102]. This separation of the protons was confirmed by ^1H NMR. The resonance lines of the water molecules were distinguished using the published atlas of crystalline hydrate spectra[107].

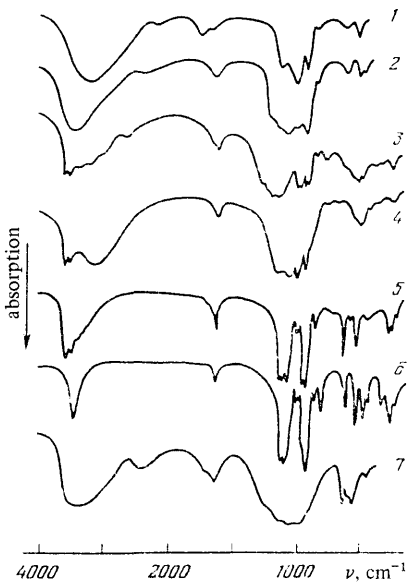
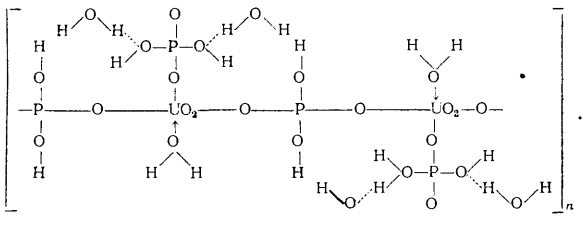


Figure 1. Infrared spectra of uranium orthophosphates: *1)* $UO_2HPO_4.4H_2O$;[64] *2)* $UO_2HPO_4.H_2O$;[64] *3)* $UO_2(H_2PO_4)_2.3H_2O$;[102] *4)* $UO_2(H_2PO_4)_2.H_2O$;[102] *5)* $(UO_2)_3(PO_4)_2.4H_2O$;[109] *6)* $(UO_2)_3(PO_4)_3.H_2O$;[109] *7)* $U(HPO_4)_2.4H_2O$.[58]

Like the monohydrogen orthophosphate, $UO_2(H_2PO_4)_2.3H_2O$ is a polymer in which one phosphate group binds the uranyl ions in a uranyl phosphate chain, while the other is terminal. One water molecule is coordinated directly to the uranium atom, and two others are joined by hydrogen bonds to $H_2PO_4^-$ groups:



The proposed scheme effectively explains the ease of hydrolysis of the dihydrogen orthophosphate with the removal of a terminal $H_2PO_4^-$ group under the influence of water and polar solvents, the reversible removal of two water molecules at low temperatures, and the decomposition of the compound when the last water molecule is removed. The coordination number of the uranyl group in this compound is probably four (the energy of the purely electronic transition is 20278 cm^{-1}[108]).

In the infrared spectrum of $(UO_2)_3(PO_4)_2.4H_2O$, the line corresponding to the $\nu_3(UO_2^{2+})$ vibrations is a doublet (Table 6)[109]. The totally symmetric $\nu_1(UO_2^{2+})$ stretch appears as a doublet. The observed splitting and activation of the $\nu_1(UO_2^{2+})$ band in the infrared spectrum indicate that the substance contains two types of uranyl group in environments with low symmetry. The nature of the absorption by the phosphate group indicates that it is extensively distorted, probably to C_{2v} symmetry. The $\nu_3(F_2)$ and $\nu_4(F_2)$ bands are split into three components[103]. The $\nu_1(PO_4^{3-})$ band is activated in the infrared spectrum. The spectra of the UO_2^{2+} and PO_4^{3-} ions of the hexahydrate are analogous to those for the tetrahydrate, although the bands are diffuse and broadened slightly. On the other hand, the spectrum of the PO_4^{3-} ion in the monohydrate (Table 6) has fewer bands, corresponding to an increase in the symmetry of this ion relative to the tetrahydrate.

Table 6. Vibrational wavenumbers (cm^{-1}) in the infrared spectra of crystalline hydrates of normal uranyl orthophosphate[109]*.

$(UO_2)_3(PO_4)_2.4H_2O$	$(UO_2)_3(PO_4)_2.4D_2O$	$(UO_2)_3(PO_4)_2.H_2O$	Assignment
217 (222)	220	225 (219)	$\delta(U{-}OPO_3)$
250	226	241 (245)	$\nu_3(UO_2^{2+})$
286 (285)	279 (289)	327	$\nu(U{-}OPO_3)$
(450)	—	428;461 (464)	$\nu_3(PO_4^{3-})$
450	375	—	$\omega(H_2O, D_2O)$
533;570 (576); 628 (625)	534;565 (575); 621 (620)	531;618 (615)	$\nu_4(PO_4^{3-})$
720 (736)	(583)	—	$\omega(H_2O, D_2O)$
852 (853,865)	850 (849,859)	804 (816);860 (850)	$\nu_1(UO_2^{2+})$
933;950	928;948	925;936;952 (950)	$\nu_3(UO_2^{2+})$
992(1002);1000(1028)	990 (1008);1000 (1031)	993 (1010);1000 (1037)	$\nu_1(PO_4^{3-})$
1076 (1105);1123; 1143 (1150)	1076 (1009);1123; 1143 (1152)	1080 (1072);1143 (1135)	$\nu_3(PO_4^{3-})$
1600;1618;1631; 1675	1126;1168;1209	1610	$\delta(H_2O, D_2O)$
3225;3325,3390; 3598;3575	2382;2498;2564; 2600;2650;2721	3450	ν(OH, OD)

* The wavenumbers found in the Raman spectra are given in brackets.

In normal uranyl orthophosphate, the PO_4^{3-} ions are probably coordinated to UO_2^{2+} as bridging bidentate anions to give uranyl phosphate layers.

The $\delta(H_2O)$ deformational wavenumbers for $(UO_2)_3(PO_4)_2.4H_2O$ indicate that the water molecules in the crystalline hydrates are non-equivalent, and the absorption at 460 cm^{-1} and 720 cm^{-1}, which is sensitive to decrease in temperature[110,111] and deuteriation ($K = 1.26$), corresponds to the librational vibrations of water.

It has been suggested[112] that the librational wavenumbers of water appear not only when H_2O is coordinated directly to the metal atom but also when a system of hydrogen bonds is formed. In the case of the tetrahydrate, however, and more particularly the monohydrate, for which the ν(OH) band has a half-width of only ~ 100 cm^{-1} with a maximum at 3450 cm^{-1}, the last effect is apparently slight. On the other hand, in the spectrum of the hexahydrate, the OH bands are broadened considerably (to 1300 cm^{-1}), apparently as a result of hydrogen bonding with excess water molecules. Analysis of the spectra indicates that in the uranyl phosphate

layer, one water molecule is coordinated to the uranyl ion, while the others are in the space between the layers.

On the whole, the spectrum of $U(HPO_4)_2.4H_2O$ shows diffuse bands due to PO_4^{3-} groups and water molecules[58] (see Table 4 and Fig.1). The ν(OH) range contains a very broad ($S_{1/2}$ = 500 cm^{-1}) band with a complex structure and maxima at 3400 cm^{-1} and 3200 cm^{-1}, against which it is possible to distinguish a band with a maximum at 2400 cm^{-1}. This band and the shoulder at 1265 cm^{-1} correspond to the P—OH stretches and deformations typical of acid phosphates[62,63].

6. Characteristic Features of the Thermal Decomposition

The thermal decomposition of the crystalline hydrates, which generally includes dehydration, depends on the state of the anion and the water molecules in the compound[5]. It was noted above that all the orthophosphates studied are three-dimensional polymers in which the PO_4^{3-} anion is coordinated to a uranium atom, and the water molecules either are mobile between the layers or complete the inner sphere of the complex. This is responsible for the great variety of forms of bonding of the water both to uranium and to the nearest groups by the formation of H-bonds of different types with the anions of neighbouring layers and with water molecules between the layers.

The dependence of the behaviour of uranyl orthophosphates when heated on these factors can be considered. The decomposition of uranyl monohydrogen orthophosphate is most complex, and shows a number of characteristic features.

1. The removal of water begins at relatively low temperatures, slightly above room temperature.
2. The dehydration of $UO_2HPO_4.4H_2O$ to the monohydrate involves a phase transformation.
3. On heating, the phosphate anion polymerises at 100° before all the water of crystallisation is removed. The quantity of polymeric forms increases with increase in temperature.
4. Up to ~ 6.5% free phosphoric acid is detected in the decomposition products.
5. Sublimation of phosphorus(V) oxide is observed at 500–600°.

The ease of removal of water is in good agreement with the assumption that the H_2O molecules lie between the layers, and with the increase in the mobility of the molecules with increase in temperature. At the same time, increase in temperature increases the probability of the movement of the protons through the system of hydrogen bonds, and in an electric field this movement becomes ordered. It may be noted that the temperature of the observed phase transformation coincides with the temperature range corresponding to the increase in the proton conductivity. A theory has been proposed[113,114] to explain the ordering of the motion of the protons in antiferroelectric orthophosphates and its relation to the phase transformation.

The increase in the mobility of the water molecules between the layers on heating may lead to the hydrolysis of the uranyl phosphate bonds and the removal of H_3PO_4 according to the schemes:

$$3UO_2HPO_4\cdot 4H_2O \rightarrow (UO_2)_3(PO_4)_2 + H_3PO_4 + 12H_2O$$

$$3UO_2HPO_4\cdot n\,H_2O \rightarrow (UO_2OH)_3PO_4 + 2H_3PO_4 + 3(n-1)\,H_2O\,. \qquad (1)$$

The concentration of free phosphoric acid reaches a maximum in the specimens heated to 150–200°. The appearance of H_3PO_4 during heating may create the impression that the increase in the electrical conductivity of the specimens is due to the electrolysis of H_3PO_4. The maximum on the electrical conductivity curve, however, does not coincide with the temperature range in which phosphoric acid is formed[70], and the conductivity in this range is low.

The formation of polyphosphates during the thermal decomposition of $UO_2HPO_4.4H_2O$ is probably the result of the superposition of a number of processes—the condensation of acid phosphate groups

$$2UO_2HPO_4\cdot n\,H_2O \rightarrow (UO_2)_2P_2O_7 + (2n+1)\,H_2O$$

and the decomposition of phosphoric acid with the subsequent reaction of pyrophosphoric acid with the components of the solid phase:

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$
$$2(UO_2)_3(PO_4)_2 + H_4P_2O_7 \rightarrow 3(UO_2)_2P_2O_7 + 2H_2O$$
$$2(UO_2OH)_3PO_4 + 2H_4P_2O_7 \rightarrow 3(UO_2)_2P_2O_7 + 7H_2O$$
$$5(UO_2)_3(PO_4)_2 + 4H_4P_2O_7 \rightarrow 3(UO_2)_5(P_2O_{10})_2 + 8H_2O \text{ etc.}$$

The reaction of H_3PO_4 with uranyl phosphates may explain the decrease in its concentration in the substance at 200–500°. Beginning at 550°, small quantities of phosphorus(V) oxide sublime into the gas phase[115].

Table 7. Stages in the removal of water from uranium orthophosphates under equilibrium conditions, and the thermodynamic characteristics of the process[116,54].

Compound	Dehydration temperature range, °C	Number of moles of H_2O	ΔH, kcal $mole^{-1}$	$\Delta S°$, e.u.
$UO_2HPO_4.4H_2O$	50—80	2.0	12.3±0.6	44.6±0.4
$UO_2HPO_4.4H_2O$	100—115	0.5	13.5±0.8	45.6±0.6
$UO_2HPO_4.4H_2O$	170—190	1.5	15.6±0.7	45.2±0.4
$UO_2HPO_4.4H_2O$	560—600	0.5	—	—
$(UO_2)_3(PO_4)_2.4H_2O$	180—210	3.0	12.0	37.3
$(UO_2)_3(PO_4)_2.4H_2O$	360—400	1.0	11.7	28.4
$U(HPO_4)_2.4H_2O$	30—150	3.0	—	—
$U(HPO_4)_2.4H_2O$	150—170	1.0	11.8	10.0
$U(HPO_4)_2.4H_2O$	180—205	0.5	38.6	33.8
$U(HPO_4)_2.4H_2O$	205—260	0.5	—	—

It was noted above that the data on the stepwise character of the removal of water and the temperature range of the dehydration given by different authors do not agree. This may be due to differences in the conditions of the experiments. To exclude the influence of such factors as the size and shape of the crystals, the rate of heating, etc., we studied[116] the thermal decomposition of the compounds under equilibrium conditions using a quartz membrane null manometer[117]. Table 7 gives data on the stepwise character of the dehydration under equilibrium conditions; it was found that it is different from that observed on heating in a stream of dry air. Throughout the entire range of temperatures studied, the anionic composition of the solid phase was restricted to ortho- and pyrophosphates (the latter was detected from 90°), whereas in the decomposition of the substance in a dry atmosphere, the heating products contained not less than six phosphate forms. A phosphorus-containing substance in concentrations of 10^{-2}–10^{-4} M was also detected in the gas phase. Increase in the water vapour pressure in the system increases the thermal stability of the substance slightly. Analysis of the infrared spectra of specimens kept under equilibrium conditions at 200° and 400° showed that the products contained uranyl hydroxo-complexes[110], whose appearance may be due to the reaction described by scheme (1). The value of $\Delta H \cong 14$ kcal $mole^{-1}$ obtained agrees with the ease of removal of water from the compound being studied, and the high value of $\Delta S°$ (45 e.u.) is apparently related to the high entropy of sublimation of water ($\Delta S°$ = 35.6 e.u.), and also to the rearrangement of the crystal

structure of the substance during the decomposition. Thus these data do not agree with the statement[119] that the atmosphere has no influence on the extent of the decomposition of the phosphate anion in bivalent metal orthophosphates.

Ammonium dioxophosphatouranate $NH_4UO_2PO_4.3H_2O$, which is isostructural with the monohydrogen phosphate, loses three water molecules in a single stage when heated, but the removal of ammonia, like that of the last water molecule from $UO_2HPO_4.4H_2O$, takes place over a wide temperature range (280–800°) and is accompanied by polymerisation of the phosphate anion[56]. The product obtained after heating was found to contain a water-soluble phosphate compound containing no uranium, and consisting of ammonium phosphate, capable of dissociating and volatilising[119]. At low heating rates, this compound dissociates, and at high heating rates it volatilises. The product of the thermal decomposition of these phosphates is a compound with the overall composition $U_2O_3P_2O_7$,[54,56] whose formation is accompanied by the liberation of oxygen and the reduction of uranium.

The thermal decomposition of the dihydrogen orthophosphate $UO_2(H_2PO_4)_2.3H_2O$, which was studied in detail by Japanese workers[120], is also complex. Since the intermediate decomposition products are metaphosphates, the authors[120] were interested in their structure. A definite relationship exists between the structure of the metaphosphates and the magnitude of the charge and size of the cation[121]; phosphates with a metal ion of medium size are cyclic, and those with very small and very large metal ions are linear. It was shown[120] that the removal of two water molecules at 120° is not accompanied by the polymerisation of the phosphate anion. Up to 300° the products are pyro-, tri-, and tetrapolyphosphates, which at a temperature above 350° are converted into linear metaphosphates according to the scheme·

$$(UO_2)_n H_2P_{2n}O_{6n+1} \rightarrow [UO_2(PO_3)_2]_n + H_2O \ .$$

In the range 900–1000°, reduction of uranium takes place, and the composition of the substance becomes simpler. The final decomposition product is uranium(IV) pyrophosphate:

$$[UO_2(PO_3)_2]_n \rightarrow nUP_2O_7 + n/2O_2 \ .$$

The anionic composition and structure of $(UO_2)_3(PO_4)_2.4H_2O$ remain unchanged on thermal decomposition up to 950°. The loss of the last water molecule begins above 330°.[54] At 950–1000°, the orthophosphate is dehydrated completely, with the simultaneous liberation of oxygen and the formation of a mixture of uranium(IV) phosphate and U_3O_8, and not a phase with the composition $U_3O_8P_2O_7$.[39] Although the heating products obtained in the range 400–800° contain small quantities of water, their spectra are practically the same as those of the monohydrate. The stepwise character of the removal of water under thermodynamically equilibrium conditions is the same as in air (see Table 7). The low values of the entropy of dehydration indicate that the changes in the structure of the substance during the thermal decomposition are slight. The oxygen pressure over anhydrous $(UO_2)_3.(PO_4)_2$ on heating to temperatures above 800° has been measured[122].

The dehydration of uranium(IV) monohydrogen orthophosphate $U(HPO_4)_2 \cdot 4H_2O$ takes place in accordance with classical ideas to give pyrophosphate according to the scheme:

$$U(HPO_4)_2 \cdot 4H_2O \rightarrow U(HPO_4)_2 + 4H_2O$$
$$U(HPO_4)_2 \rightarrow UP_2O_7 + H_2O \ .$$

UP_2O_7 crystallises at ~ 760°.

Shchegrov[118] reviewed published data on the regular features of the mechanism of the dehydration of bivalent metal orthophosphates on the basis of the state of the water molecules present, in particular the strength of the hydrogen bonds with the phosphate anion. The dehydration of both acidic and normal orthophosphates takes place in three stages[118].

The first stage takes place at relatively low temperatures, and is accompanied by the removal of water molecules forming relatively weak hydrogen bonds with the anion, with energies up to 7–8 kcal mole^{-1}:

$$M_3(OH_2)_x(PO_4)_2(m-x)H_2O \rightarrow M_3(OH_2)_x(PO_4)_2 + (m-x)H_2O$$
$$[M(OH_2)_x HPO_4](m-x)H_2O \rightarrow [M(OH_2)_x HPO_4] + (m-x)H_2O \ .$$

The second stage, the removal of more firmly bound water (with hydrogen bond energies of 9–11 kcal mole^{-1}), is accompanied by extensive structural transformations such as the formation of a mixture of higher phosphates, hydroxides, or oxides of the metal:

$$n/2M_3(OH_2)_x(PO_4)_2 \rightarrow M_{(n+2)/2}P_nO_{3n+1} + (n-1)M(OH)_2 + \frac{nx-2n+2}{2}H_2O$$
$$n[M(OH_2)_xHPO_4] \rightarrow M_{(n+2)/2}P_nO_{3n+1} + \frac{n-2}{2}MO + \frac{n(2x+1)}{2}H_2O \ .$$

The third stage gives an intermediate dehydration product with a simpler composition, as a result of the following reactions:

$$M_{(n+2)/2}P_nO_{3n+1} + (n-1)MO \rightarrow \frac{n}{2}M_3(PO_4)_2$$
$$M_{(n+2)/2}P_nO_{3n+1} + \frac{n-2}{2}MO \rightarrow \frac{n}{2}M_2P_2O_7 \ .$$

The data in Refs.118 and 123–127 show some lack of agreement. Analysis of the infrared spectra of the dehydration products shows that the specimen first loses the water joined by "strong hydrogen bonds" (ν(OH) = 3030–3060 cm^{-1})[123–125], whose energy was estimated as 35–40 kJ mole^{-1}. At the same time, the high-wavenumber vibrations of the water molecules (above 3400 cm^{-1}, bond energies 10–15 kJ mole^{-1}) are preserved in the spectrum, while the OH stretching bands show an overall decrease in width. These bands generally remain in the spectrum up to fairly high temperatures.

In the discussion of the spectra in Refs.126 and 127, no account was taken of the possibility of the direct coordination of the phosphate group to the metal. Ideas about the aquocomplexes of a number of isostructural sulphates and perchlorates of bivalent metals (Co, Ni, Fe, Zn, Ca, Mg)[128,129], in which the water molecules are in the inner coordination sphere, and the anion is in the outer sphere and forms H-bonds with the water molecule, were applied to the phosphates. X-ray diffraction data on the phosphates of Ca^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, Mg^{2+}, Al^{3+}, etc.[130–137] have shown that they are three-dimensional polymers, in which the polyhedron around the metal atoms is formed by the oxygen atoms of phosphate groups. The water molecules in hydrates with low water contents can act as bridges between metal atoms[131] or be coordinated to the metal or situated in the space between the layers[138,139], being held in the crystal lattice by hydrogen bonds. X-ray diffraction data indicate that the strength of the bonding of the water on dehydration is determined by the structure of the phosphate. The coordinated water molecules are naturally held much more strongly, as confirmed by the measured M–O(H_2O) bond lengths, which are equal to 2.0–2.2 Å and are comparable with the M–O(PO_4) distance. The formation of H-bonds with the outer-sphere anion will increase the force constant of the M ← OH_2 bond.

When extremely strong symmetrical H-bonds O...O with length 2.4–2.6 Å, which are formed extremely rarely in crystals, are produced, ν(OH) may reach 3000 cm^{-1} or less. When estimating the energy of hydrogen bonds from the lowering of the ν(OH) vibrational wavenumbers, however, care must be taken, since it is necessary to make allowance for a number of factors which displace the ν(OH) wavenumber in the same direction as hydrogen bonding. On coordination,

the displacement of ν(OH) to lower wavenumbers may reach 600 cm^{-1}, and it is complex in character and does not always depend on the strength of the bond formed with the metal. The displacement is also determined by the symmetry of the molecule, the perturbing influence of the field of the central atom, the nature of the hybridisation of the orbitals, Fermi resonance, etc.[140-143] The nature of the bonds formed by water is best deduced from the librational wavenumbers[141-143]; the wavenumbers of the rocking and wagging vibrations increase with increase in the strength of the M ← OH_2 bond.

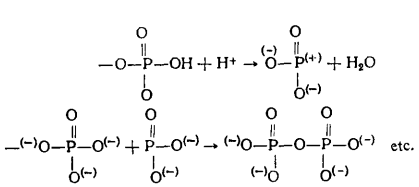
It is clear from the foregoing that without a knowledge of the structure of the compound, the estimation of the perturbing influence of the anion on the water molecules from the displacement of the ν(OH) wavenumbers is inaccurate. The situation is complicated by the fact that even in the anhydrous acidic compounds[132,138,144,145], the proton of the phosphate group is involved in a system of H-bonds with neighbouring layers, and in the case of the crystalline hydrates, the number of possible hydrogen bonds increases sharply.

Returning to the uranium phosphates, it can be seen that the dehydration of uranyl monohydrogen orthophosphate, which contains mobile water between the layers, involves the production of up to six forms of polyphosphate and free phosphoric acid, whose formation in the decomposition of bivalent metal phosphates has been related[118,123-127] to the existence of strong hydrogen bonds between the coordinated water molecules and the outer-sphere phosphate anion.

It can be seen from the case of $UO_2HPO_4.4H_2O$ that it is probably premature to reject the possibility of hydrolysis to explain the thermal decomposition of phosphates, particularly in view of the fact that many phosphates contain mobile water between the layers. On the other hand, in the decomposition of the normal orthophosphate monohydrate, which contains coordinated water (ν(OH) = 3450 cm^{-1}), the H_2O molecules are removed gradually up to a temperature of 900°, and polymeric forms of phosphate were not detected in the dehydration products. On the other hand, uranium(IV) monohydrogen orthophosphate, which gives extremely broad ν(OH) bands with a maximum at 3200 cm^{-1}, indicating strong hydrogen bonding, decomposes in accordance with classical ideas to uranium pyrophosphate.

Thus the ideas developed in Refs.5, 118, and 123–127 do not make possible a sufficiently reliable explanation of the mechanism of the dehydration of uranyl and uranium orthophosphates. A preferable concept was developed by the authors of Refs.146–149, who regard all crystalline hydrogen phosphates as proton semiconductors, which when heated above a definite temperature give free protons, capable of moving easily through interstices in the crystal lattice. The concentration of this "proton gas" increases with increase in temperature; the probability of its reaction with the phosphate tetrahedra also increases.

The condensation takes place by a series of successive processes involving ionisation of anionic sites:



The proton transfer is most effective when the compound contains a system of hydrogen bonds, and the degree of transfer depends on the crystal structure of the compound. With the formation of hydrogen orthophosphates, an increase in the strength of the P–OH bond and a decrease in the strength of the PO–H bond compared with the HPO_4^{2-} anion are assumed. The formula $[...(M-O)_3-P=O]^-H^+$ has been proposed to describe the structure of group IV metal phosphates[150].

III. CONDENSED URANIUM PHOSPHATES

A review of uranium phosphates would be incomplete without an examination of polymeric phosphates with different degrees of condensation. Uranium pyrophosphates in solution were studied in Refs.151–155, where it was shown that the reaction of uranyl nitrate with sodium pyrophosphate gives cationic complexes $[(UO_2)_nP_2O_7]^{2(n-1)}$, where n = 3–5. The composition of the pyrophosphates depends on the medium. The insoluble complex $[Na_4(UO_2)_8(P_2O_7)_5]$ and the soluble complexes $[Na_2UO_2P_2O_7]$, $Na_6UO_2(P_2O_7)_2$,[151] and $[UO_2H_q(P_2O_7)_x]^{(4x-q-2)-}$ (x = 1,2) were detected. At pH 0.83–3.00, $[(UO_2)_5H_2P_2O_7]^{8+}$ is formed[153]. Uranyl pyrophosphates including heavy metal cations (Ag^+, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}) have been prepared[155]. The possible formation of the uranyl hydroxide pyrophosphate $(RNH_3)_3UO_2OHP_2O_7$ in the extraction of uranium(IV) from pyrophosphate solution by alkylamines has been suggested[156].

The $UO_2(NO_3)_2$–$Na_4P_2O_7$–H_2O system has been studied[157], and the following salts isolated: the soluble $Na_6UO_2(P_2O_7)_2.6H_2O$ and the insoluble $Na_2UO_2P_2O_7.3H_2O$, $Na_2UO_2P_2O_7.2H_2O$, $Na_2(UO_2)_3(P_2O_7)_2.5H_2O$, and $(UO_2)_2P_2O_7.4H_2O$. Secondary processes gradually take place in the system, but their nature was not established[157].

The $Na_4P_2O_7$–$UO_2(NO_3)_2$–H_2O system was studied by the present authors by measuring the electrical conductivity, pH, and refractive index of isomolar series at concentrations of 0.001–0.2 M[158]. The existence in solution of complexes with ratios $P_2O_7^{4-}$:UO_2^{2+} of 2:1, 1:1, 1:2, and 1:6 was detected (some of these complexes were reported earlier[151,157]). To isolate the solid compounds, they were synthesised by mixing solutions to give the above component ratios. The pyrophosphates $Na_6UO_2(P_2O_7)_2.3H_2O$, $Na_2UO_2P_2O_7.5H_2O$ and $(UO_2)_2P_2O_7.8H_2O$ were obtained. The first of these is readily soluble in water, and it was salted-out with acetone or ether and dried in a desiccator over phosphorus(V) oxide. The pyrophosphate with ratio 1:6 could not be obtained[158]. When solutions to give this ratio were mixed, the precipitate, which formed 24 h after the solutions were mixed, contained up to 30% of the ortho-form. When the solutions were kept for a long time, the specific conductivity and refraction curves showed a displacement of some of the maxima, and in an excess of the uranyl ion (ratio > 1:2), changes were also observed visually; the external appearance and volume of the precipitates altered. To determine the reasons for these changes, the pyrophosphates were kept in equilibrium with the solution and then analysed by chromatography. After one month, the 1:1 and 1:2 compounds contained appreciable quantities of orthophosphate (~ 14 and 27), and at a ratio of 1:6 the system contained no pyrophosphate, and the precipitate consisted of $(UO_2)_3(PO_4)_2.4H_2O$.

Thus uranyl pyrophosphates in solution undergo appreciable degradation, which increases with increase in the uranium concentration. Thus the changes detected[157] in the system result from the decomposition of the polyphosphate anion. It was important to determine whether analogous degradation of the anion takes place in the solid phase. The chromatographic data showed that one month after the formation of the 2:1, 1:1, and 1:2 compounds, the first contained practically no ortho-form, and the others ~ 10% and 25% PO_4^{3-} respectively.

The $Na_4P_2O_7$–$UO_2(NO_3)_2$–H_2O system was also studied by other workers[159], who isolated the 1:1 and 1:2 complexes. The preparation of the 2:3 compound $Na_2(UO_2)_3(P_2O_7)_2.14H_2O$ has been reported[158]. The individuality of the last compound is doubtful, since its composition is extremely sensitive to slight changes in the $P_2O_7^{4-}$:UO_2^{2+} ratio in the solution[158]. The infrared spectrum and heating curves of the product[159] are practically the same as those of the 1:1 compound. The authors[159], in spite of the reported[158] possibility of the degradation of uranyl pyrophosphates, studied the equilibrium in the system over a prolonged period. It will be shown below that with increase in the length of the polyphosphate chain, the ability of the uranyl phosphates to undergo degradation increases. The composition and structure of the compounds crystallising from melts of the $(UO_2)_2(P_2O_7)$–$Na_4P_2O_7$ system have been studied[160].

In the $Na_5P_3O_{10}$–$UO_2(NO_3)_2$–H_2O system, compounds with $P_3O_{10}^{5-}$: UO_2^{2+} ratios of 2:1, 1:1, 1:3, 3:5, 1:2, and 2:5 exist in solution[161]; some of these compounds were reported earlier[162–166]. The ranges of stability of the crystalline hydrates of uranyl tripolyphosphates were determined by the present authors, and the following solid compounds isolated[161]: $Na_3UO_2P_3O_{10}.6H_2O$, $Na_4(UO_2)_3(P_3O_{10})_2.14H_2O$, $Na_5(UO_2)_5.(P_3O_{10})_3.22H_2O$, $Na(UO_2)_2P_3O_{10}.9H_2O$, and $(UO_2)_5(P_3O_{10})_2.21H_2O$.

The 1:1 and 2:5 compounds are obtained even with slight variation in the ratios of these components, but the 2:3, 3:5, and 1:2 complexes have these compositions in the solid state only with the appropriate stoichiometry in the solution.

The characteristics of the vibrational spectra of uranyl tripolyphosphates have been discussed[167]. On going from the 1:1 to the 2:5 compound, the $\nu_{as}(=PO_2)$ stretching wavenumbers tend to decrease from 1240 cm^{-1} to 1210 cm^{-1}, and $\nu_{as}(PO_3)$ from 1165 cm^{-1} to 1155 cm^{-1}. This can apparently be related to an increase in the degree of polymerisation of uranyl tripolyphosphates. A gradual increase in the strength of the binding of the water molecules in the complexes is observed in the same order (1:1 < 2:3 < 3:5 < 1:2 < 2:5). This can be seen from the thermal analysis data: water is removed at ~ 300° from the 1:1 compound, 500° from the 2:3 and 3:5 compounds, 700° from the 1:2 compound, and only at 800° from the 1:5 compound. The melting points of the dehydration products increase in the same order: the 1:1, 2:5, and 3:5 complexes melt in the range 800–850°; the 1:2 compound at 1150°, and the 2:5 compound at 1200°. On the other hand, the tendency of uranium to be reduced decreases: reduction takes place at 900° for the 1:1 complex, and at 700° for the 1:2 and 2:5 complexes. The final product of the thermal decomposition of uranyl polyphosphates at 1000° is a mixture of linear phosphates.

When considering the thermal stability of uranyl phosphates, mention must be made of the final decomposition products. The possibility of determining uranium as phosphates has been discussed many times. Different forms to be weighed have been proposed by different authors: $U(PO_3)_4$,[168] $U_2O_3P_2O_7$,[169–171,29] and $U_2O_5P_2O_5$.[172] In the description of the thermal stability of uranium orthophosphates, it was shown that the final decomposition products of the phosphates have different overall compositions. The decomposition products of the polyphosphates also have a different composition. The final products often contain a mixture of phosphates with different anionic compositions; the identification of the products is also complicated by the reduction of uranium on heating. Care must therefore be taken in the analytical determination of uranium by the published methods[29,169,171], and it should be remembered that the overall composition of the products formed on heating depends on the composition of the original specimen.

The tripolyphosphates, like uranyl pyrophosphates, are unstable when left to stand; Fig.2 illustrates their degradation at 0° and 25°. It can be seen from Fig.2 that the tendency to undergo degradation decreases with decrease in temperature. Unlike the pyrophosphates, for which the degree of degradation increases with increase in the uranium concentration, the degree of degradation of the tripolyphosphates shows a complex dependence on composition. In the series of compounds with the 1:1, 2:3, and 3:5 compositions, the degradation of the anion increases (the $P_3O_{10}^{5-}$ concentration after 100 d at 25° was 55, 25, and 5% respectively), whereas the 1:2 and 2:5 complexes after the same time interval contained 15% and 35% $P_3O_{10}^{5-}$.[173] In the 2:3 and 3:5 compounds there is probably considerable deformation of the phosphate anion. Thus the tendency of uranyl polyphosphates to undergo degradation increases with increase in the length of the phosphate chain, and depends on the structure of the phosphate. More complex linear polyphosphates should probably be even less stable.

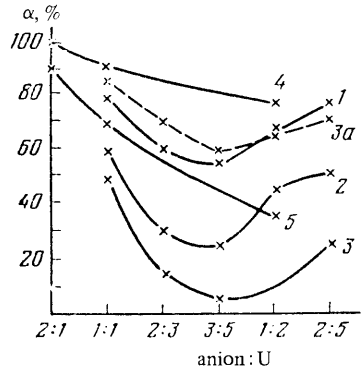


Figure 2. Dependence of the degree of degradation of uranyl pyro- and tripolyphosphates on the time for which they have been kept: *1, 2, 3*) tripolyphosphates at 25 °C after 10, 30, and 100 d respectively; *3a*) tripolyphosphates at 0 °C after 100 d; *4, 5*) pyrophosphates after 30 d; α is the concentration of the original phosphate[158,161].

In the discussion of the degradation of phosphate anions, it should be noted that there are practically no published data on the decomposition of solid polyphosphates. The dependence of the degradation of polyphosphates in solution on the pH of the medium and temperature has been studied[174,176]. It was shown only recently[177,178] that like uranyl phosphates, the tripolyphosphates of Co^{2+}, Ni^{2+}, and Cu^{2+} undergo degradation in the solid phase, the extent of the decomposition being greater for the copper phosphate.

Uranyl metaphosphates are much more stable than the polyphosphates. Japanese workers[179] have shown that uranyl tetrametaphosphate is more stable than the trimetaphosphate with respect to hydrolysis in the presence of UO_2^{2+} ions. α- and β-$U(PO_3)_4$ have been obtained and identified by X-ray diffraction[180].

The study of condensed uranyl and uranium phosphates was extended by Soviet workers[181–185]. The crystalline condensed phosphates formed in the UO_2–P_2O_5–H_2O and UO_2–P_2O_5–M_2O–H_2O systems (M = alkali metal), which contain

molten polyphosphoric acids, were synthesised and studied. The conditions of formation and crystallisation of the phosphates $UO_2(PO_3)_2$, $UO_2H(PO_3)_3$, and $(UO_2)_2P_6O_{17}$ were determined[181]. The synthesis of the hydrogen phosphate stimulated the search for analogous compounds with alkali metal ions, of the type $MUO_2(PO_3)_3$, where M = Na, K, Rb, or Cs; their optimum crystallisation temperature is 320°.[181]

$UO_2H(PO_3)_3$ is made up of spiral polyphosphate chains $[H_2P_6O_{18}]^{4-}$ of six PO_4^{3-} tetrahedra, extending along the (100) direction, and joined by uranyl ions to form a three-dimensional framework[183].

The behaviour in a melt of the uranyl ion with the cations Sr, Ba, and Pb, and oxocations MO_2^{2+}, has been compared[181]. Uranyl cations and the cations of these metals form ultraphosphates $M^{II}{}_2P_6O_{17}$.

The possibility of obtaining the metaphosphate $U(PO_3)_4$ by the reaction of metallic uranium or $UO_2(NO_3)_2.6H_2O$ with a melt of 87% H_3PO_4 in the presence of $NH_4H_2PO_4$ (which accelerates the reduction of UO_2^{2+} to U^{4+}) has been studied[184,185]. $U(PO_3)_4$ crystallises in two forms. The compound $U(PO_3)_4$(I) has a structure analogous to the zirconium phosphate structure. It consists of a framework of $[UO_8]$ eight-apex polyhedra and chains of PO_4 tetrahedra cross-linked into double spirals. The structural analysis of metaphosphates makes it possible to regard all uranyl phosphates as polymers with a uranyl phosphate framework in which the water molecules and other metal ions are situated in the space between the layers. In a number of phosphates, the water molecules are coordinated directly to the uranium atom.

Uranyl phosphites $UO_2HPO_3.3H_2O$,[186] $M_2UO_2(HPO_3)_2$ (M = Na, K, NH_4),[187] and the products of the reaction with amides[188] are also polymeric. The uranium(IV) phosphites $U(HPO_3)_2.2H_2O$ and $U(H_2PO_3)_4$[189] have also been obtained.

The reduction of $UO_2(PO_3)_2$ and vitreous $UO_3.1.5P_2O_5$ by hydrogen has been studied[190]. It is suggested that the reduction takes place according to the scheme:

$$UO_2(PO_3)_2 \xrightarrow{450-600^\circ} \rightrightarrows P_2O_7\ \text{(cubic)} \rightarrow UP_2O_7\ \text{(orthorhombic)} \rightarrow (UO_2)_2P_2O_7 \rightarrow U_8O_{13}.$$

Cubic UP_2O_7 is stable up to 1000°. In $NaPO_3$–NaCl melts at 700–900° in the range rich in sodium metaphosphate, favourable conditions are created for the rapid solution of the sparingly soluble oxide UO_2.[191] The mechanism of the reaction in the system, and the form of the phosphate obtained, were not studied, however[191].

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The material examined deals with the synthesis of uranyl and uranium phosphates, the problems of studying their behaviour in solution, the stability of the crystalline hydrates, and the stability of the phosphate anion with increase in the length of the phosphate chain. Study of the thermal decomposition has shown that the behaviour of the compounds in these processes is determined by their structure and the mode of binding of the phosphate anion and the water molecules. When uranium phosphates contain mobile water molecules and protons, the decomposition processes become more complex: polymerisation of the phosphate anion, liberation of H_3PO_4, etc.

The study of uranium phosphates is opening up new possibilities for their further use in electrochemical devices, for dissolving sparingly soluble oxides, and also to solve the problems of improving the technology of the extraction of uranium from phosphate raw material, which is now acquiring increasing importance as rich uranium ores become exhausted. In the production of phosphoric acid by extraction, methods have been developed which make it possible to extract up to 10% of the total uranium produced[192–199].

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Kinetics and Mechanism of the Dissolution and Oxidation of Semiconductors

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A generalised kinetic approach to the description of the dissolution of semiconductors (including the thermal oxidation of silicon and germanium) is based on a statistical thermodynamic analysis of the adsorption steps, and on an analysis of the structure of the activated complex and of the effects of solvation of the intermediate and the final products (calculated from model descriptions). 66 references.

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I. INTRODUCTION

Academician Ioffe once wrote: "The most important property of semiconductors, which determines their behaviour and their suitability for various applications, is the nature of their chemical bond"[1]. The interaction between nearest neighbours has been used as a basis for classifying electronic, optical, and kinetic processes in semiconductors as well as in various vitreous solids[2,3]. This justifies the present attempt to analyse data on the kinetics of chemical dissolution reactions and of oxidation processes on semiconductor surfaces, aimed at identifying the main features of the elementary steps which play an important role in the transfer of an atom from the semiconductor to the adjacent gaseous or condensed phase as a result of chemical interaction[4-8]. We shall show that in spite of differences in the detailed chemistry of these phenomena the elementary acts which control the dissolution and oxidation processes are basically similar.

Once the basic characteristics of the elementary steps are known, a kinetic model of the overall multi-step process can be constructed, allowing for the special features of the reacting system: for example, a model for analysing the kinetics of semiconductor oxidation processes. A large amount of experimental information on the properties of the silicon–silica interface is now available. However, since these studies describe the system *a posteriori*, they do not allow the processes taking place at the semiconductor–dielectric interface during the oxidation to be reconstructed unambiguously. The approach suggested here offers entirely new possibilities for studying and controlling the properties of this interface.

II. DEFINITION AND CLASSIFICATION OF DISSOLUTION REACTIONS

In general, the term dissolution reaction describes a process at a phase boundary which results in the transfer of atoms or structural units from a crystal (or other solid) to the surrounding medium as a consequence of their chemical interaction with the active components of the neighbouring phase[9]. The chemical interaction can be treated in as much detail as in the molecular theory of solutions[10-12]. The dissolution reactions can be described as solvating, oxidising, or oxidising–solvating. The solvating type includes the reactions which cause the dissolution of ionic crystals in polar solvents, and also the dissolution of solids in melts. All other dissolution processes are either oxidising–solvating or oxidising.

Dissolution reactions can be classified (according to the type of phases in contact) as dissolution into a gas, a liquid, or a solid phase. Of course, reactions leading to dissolution into a gas phase are an example of oxidative dissolution. Reactions leading to dissolution into a condensed phase are the most complex type of oxidative–solvating interaction.

III. KINETIC MODEL

Like all heterogeneous reactions, the dissolution reaction is the result of a succession of elementary steps: adsorption of the active reactant, chemical conversion in the adsorption layer, and desorption of the product (with a corresponding reorganisation of the element of volume of the condensed phase in the interfacial region)[13-15]. This sequence of elementary acts can be described by the series of steps

$$A_2^{(II)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_2^{(s)} \qquad (1)$$

$$A_2^{(s)} \underset{k_{-1}'}{\overset{k_1'}{\rightleftarrows}} 2A^{(s)} \qquad (1')$$

$$A^{(s)} + U^{(I)} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} UA^{(s)} \qquad (2)$$

$$UA^{(s)} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} UA^{(II)} \qquad (3)$$

Eqns.(1) and (1') describe the adsorption on the crystal surface (phase I) of the molecule A_2 in the surrounding phase II. In general, adsorption is a two-step process in which k_1 is the rate constant for the adsorption of the intermediate molecular form and k_1' is the rate constant for the dissociative adsorption step. In most cases the adsorption process is accompanied by a structural rearrangement of the near-surface region of the crystal. Eqn.(2) defines the step (chemical reaction in the adsorption layer) in which the

adsorbed particle $A^{(s)}$ reacts with an atom or with a structural unit of the crystal ($U^{(I)}$) to form an adsorbed particle of the reaction product $UA^{(s)}$. The last step corresponds to desorption of this particle and formation of the final reaction product in the near-surface region of phase II: $UA^{(II)}$.

The kinetic analysis of this sequence of steps is not difficult. We shall confine our discussion to reactions in systems far from thermodynamic equilibrium and ignore the reversibility of step (2), i.e. we shall put $k_{-2} \cong 0$. This condition cannot apply at the boundary between a crystal and its melt, or to the dissolution of a semiconductor in the gas phase at high temperature, when crystal growth and crystal dissolution processes take place at comparable rates.

In our model the rate of the dissolution process (w_2) can be written

$$w_2 = k_2 \frac{k_1}{k_{-1}} [A_2^{(II)}] / \left(1 + \frac{k_1}{k_{-1}} [A_2^{(II)}] + \frac{k_2}{k_{-1}}\right) . \quad (4)$$

Two important special cases can be defined. In the first, the adsorption rate constant for the irreversible chemisorption of the reactant A_2 is much smaller than the rate constant of reaction (2): $k_2 > k_1 \gg k_1$, and therefore

$$w_2 = k_2 \alpha [A_2^{(II)}] / (1 + \alpha [A_2^{(II)}]) , \quad (5)$$

where $\alpha = k_1/k_2$. In the second case the adsorption step is reversible, i.e. $k_{-1} \gg k_2$, and

$$w_2 = k_2 a [A_2^{(II)}] / (1 + a [A_2^{(II)}]) , \quad (6)$$

where $a = k_1/k_{-1}$.

The equations describing these two cases are formally identical, but the physical significance of the parameters is entirely different in the two cases. The case described by Eqn.(5) is typical of oxidative dissolution only. On the other hand Eqn.(6) corresponds to kinetics of the Langmuir type, and it applies both to oxidative and to oxidative–solvating dissolution.

These two possible alternatives of our kinetic model of the dissolution process lead to the following conclusions. In the region of low concentrations of the reactant A_2 the reaction is always of the first order with respect to the active molecules. However, in the first variant [Eqn.(5)] the reaction rate is determined by the rate of the adsorption step. We should stress that the experimental value of the activation energy corresponds to the activation energy for adsorption, and the pre-exponential factor is $C_T = k_{01}$. The parameter k_{01} can be calculated from model considerations of the adsorption complex[13–15]. In the second variant [Eqn.(6)] the activation energy found experimentally in the region of first-order kinetics is $E_{exper} = H_2^{\neq} - \Delta H_{ads}$ (where $H_2^{\neq}$ is the activation energy of step (2), and ΔH_{ads} is the heat of adsorption), and the pre-exponential factor is $C_T = a_0 k_{02}$. Usually $k_{02} = n_S \nu$, where n_S is the density of surface atoms (or structural units), and ν is the frequency of their thermal vibrations. Statistical mechanical calculations gave values of a_0 in the range of 10^{-14}–10^{-13} for the immobile adsorption state and 10^{-8}–10^{-4} Torr^{-1} for mobile adsorption.

At high concentrations of the reactant A_2 the reaction is kinetically of zero order. In both variants the experimental activation energy corresponds to the parameter $H_2^{\neq}$, and the pre-exponential factor is usually $C_T = n_S \nu$. By analysing the experimental kinetic and thermodynamic data for the oxidative dissolution of semiconductors we conclude that the main exothermic effect of the reaction is contributed by the chemisorptive interaction between the active molecule and the crystal surface. Often the heat of chemisorption is greater than 20 kcal mole^{-1}, and the energy released in the adsorption interaction step makes possible the rearrangement of the short-range order region surrounding the given surface atom. Under these conditions the kinetics of the dissolution reaction are no longer affected by the crystallographic orientation, as has been demonstrated for the interaction of germanium with H_2S, S_2, and Br_2,[13–15] with O_2,[16] and for the interaction of silicon with O_2.[17]

When the heat of adsorption is a few kcal mole^{-1}, as in the interaction of silicon and germanium with their tetra-halogen derivatives[15,18], the dissolution usually takes place in the region of low surface coverage and is kinetically of the first order with respect to the reactant. This usually implies a dependence of the heat of adsorption, and therefore also of the activation energy of the dissolution reaction, on the orientation of the crystal.

IV. SPECIAL FEATURES OF SEMICONDUCTOR DISSOLUTION REACTIONS IN A CONDENSED MEDIUM

Adsorption processes associated with dissolution reactions have a number of special features. If the heat of dissolution of the A_2 active molecules in the condensed phase is $\Delta H_{diss}^{(II)}$, their heat of adsorption on the semiconductor surface is

$$\Delta H_{ads}^{K} = \Delta H_{ads} - \Delta H_{diss}^{(II)} . \quad (7)$$

The special case of $\Delta H_{ads} = \Delta H_{diss}$ can occur. In this case there is no surface excess of component A_2, and the reaction takes place by simple collisions between the A_2 particles and the surface. There is an analogous case in the kinetics of catalytic reactions (the Eley–Rideal mechanism). This type of dissolution reaction was originally proposed by Myuller[19]. We conclude that in oxidative–solvating dissolution reactions the contribution from adsorption interactions to the observed activation energy is small (or even zero) as compared with gas-phase reactions.

The coefficient a_0^K which appears in the expression for the pre-exponential factor can be calculated by a model approach[20,21]. The simplest involves the assumption that the molecules of the active component A_2 occupy holes of linear dimension d in the condensed phase, and that when these molecules are transferred to a cell immediately adjacent to the crystal surface they lose one translational degree of freedom and become adsorbed according to Eqn.(1). In this case

$$a_0^K = h/(2\pi MRT)^{1/2} d , \quad (8)$$

where h and R are Planck's and Boltzmann's constant (the gas constant here Ed. of Translation), and M is the molecular weight of the A_2 particle. A typical value of a_0^K is 1×10^{-2} cm^3 mole^{-1}.

Allowance for the adsorption of solvent molecules (as well as that of the A_2 molecules) is often needed when the dissolution medium is highly polar[8,22]. This means that the reaction rate is proportional to the product of the surface coverages by reactant molecules (θ_{A_2}) and by molecules of the polar solvent (θ_L):

$$w_2 = k_2 \theta_{A_2} \theta_L . \quad (9)$$

V. ATOMIC AND ELECTRON–ION SUBSYSTEMS IN THE DISSOLUTION PROCESS

The dissolution of a semiconductor is usually assumed to occur by two processes taking place in parallel (either independent, or conjugated): the delocalised interaction of the solid with the oxidiser and solvating agent particles (electrochemical mechanism) and the localised interaction of the

oxidiser with an active surface complex (chemical mechanism)[23–26]. We have shown[4,6,8] that in most cases the kinetics of the dissolution process are determined by the local aspects of the interaction between the oxidiser particles and the active surface complex. Though a strict calculation of the exchange currents for the electron–ion and atom–ion subsystems of the semiconductor has not yet been attempted, a qualitative comparison of semiconductors and metals can be based on experimental data.

The exchange currents for the electron–ion reactions Fe^{3+}/Fe^{2+} and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ on a metallic electrode are known[26] to be 5×10^{-3} and 10 A cm^{-2} respectively. From the relationship between the exchange currents i_0^M and i_0^S for a metallic and semiconductor electrode (which are determined by the width of the forbidden energy gap E_g [27])

$$i_0^S = i_0^M \exp(-E_g/4RT) \qquad (10)$$

we find that for a typical semiconductor with a forbidden gap 0.75 eV wide the exchange currents of these electron–ion reactions are 10^{-6} and 10^{-2} A cm^{-2} respectively. Our study[28] of the temperature dependence of the anodic dissolution of germanium gave an exchange current of 10^{-10} A cm^{-2} (at 25 °C) for the exchange current of the atom–ion subsystem.

These numerical results confirm the conclusion that equilibrium in the electron–ion subsystem is established easily and rapidly at the semiconductor–electrolyte interface. In this sense the atom–ion subsystem is the slow system[29]. Thus we must examine the effects arising from two subsystems (electron–ion and atom–ion) in order to describe the dissolution of semiconductors in polar media. We have also shown[23] that the step in which the oxidiser particles interact with the crystal can be assumed to have reached equilibrium (including the injection of positive holes into the semiconductor as a result of electron transfer between the crystal and the oxidiser). It follows that the potential difference at the semiconductor–electrolyte interface ($\Delta\phi$) is determined by the constants of the adsorption equilibrium steps (1) and (1′).

If γ is the fraction of the potential drop $\Delta\phi$ corresponding to the Helmholtz layer, the activation energy of reaction (2) depends on the potential in the normal way[24]. The fraction of the potential $(1 - \gamma)$, associated with the space charge layer, affects the exchange current of the atom–ion subsystem (see Ref. 24). The establishment of thermodynamic equilibrium at the adsorption interaction step assists the electron transfer processes between the bands (valence, and conduction) of the semiconductor and the Red–Ox system of the solution (as was first pointed out by Gerischer[25]).

VI. STRUCTURE OF THE ACTIVATED COMPLEX

The structure and the characteristics of the activated complex can be determined strictly by calculating the profile of the potential surface for the system of interacting atoms. Recent advances in computational methods of quantum chemistry have made these calculations possible for some of the simpler systems. However, for the reactions being discussed here the calculations cannot be strict, but though the analysis is only qualitative it leads to some definite conclusions.

The special properties of the potential energy curves are identified by comparing the thermodynamic and the kinetic characteristics. The total enthalpy change of the reaction

$$\tfrac{1}{2}A_2 + U = UA(g) \qquad (11)$$

is

$$\Delta H = \tfrac{1}{2}(\Delta H_1 + \Delta H_{1'}) + \Delta H_2 + \Delta H_3 , \qquad (12)$$

where ΔH_1, $\Delta H_{1'}$, ΔH_2, and ΔH_3 are the enthalpies of steps (1), (1′), (2), and (3) respectively.

For exothermic reactions we have $\Delta H < 0$. It follows from published data[6,9,13,16,20] that for dissolution reactions giving rise to bivalent germanium and silicon products we can write

$$|\Delta H_2 + \Delta H_3| \simeq H_2^{\neq} , \qquad (13)$$

whereas for reactions in which quadrivalent compounds are formed

$$|\Delta H_2 + \Delta H_3| < H_2^{\neq} . \qquad (14)$$

From these expressions we note that reactions in which bivalent compounds are formed are barrierless, whereas reactions in which quadrivalent compounds are formed have an energy barrier (see Fig. 1). A barrierless reaction path indicates a smooth change in the structure of the activated complex from the state corresponding to the potential energy minimum to that of the final product. The presence of a barrier leads to the formation of a special type of complex which rearranges itself into the final product. Often the life-time of this complex is greater than 10^{-12} s, and in this case the formation of an intermediate product becomes possible.

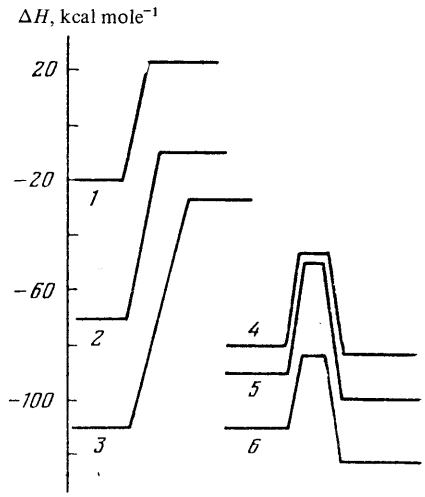
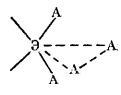


Figure 1. Examples of barrierless reactions [U + $1/2A_2$ = UA(g); U = Ge (*1, 2*) or Si (*3*), $A_2 = S_2$ (*1*) or O_2 (*2, 3*)] and of barrier reactions [U + $2X_2$ = UX_4(g); U = Ge (*4, 6*) or Si (*5*), $X_2 = Br_2$ (*4, 5*) or Cl_2 (*6*)].

We have previously studied[6] the nature of the activated complex for the formation of GeS by the interaction of Ge with H_2S and S, and we have shown that it has the Ge_2GeS structure, in which the germanium–sulphur bond is multiple but the two germanium–germanium bonds are weakened simultaneously as the GeS particle moves away from the surface. The displacement on activation amounts to 1.5–2.0 Å.

Dissolution reactions involving the formation of quadrivalent products take place by a barrier mechanism, and Eqn. (14) applies to these reactions. This conclusion was confirmed for the interaction of germanium and silicon with Cl_2 and Br_2.[15] In these reactions the activated complex has the structure



in which the A atoms are located at the corners of a distorted tetrahedron and the displacement of the semiconductor atom U on activation corresponds to the distortion of the bonds between the semiconductor atom and its nearest neighbours, and is therefore assisted by the insertion of the U atom into the centre of the tetrahedron.

The barrier mechanism is typical of dissolution reactions involving polar solvents. In these cases the donor–acceptor interaction of the adsorbed polar molecules of the solvent assists the formation of the tetrahedrally coordinated complex.

The kinetic characteristics of semiconductor gas-phase dissolution reactions are the simplest and the most accurately calculable. These can be treated as model reactions, and their kinetic parameters can often be used to establish the characteristics of reactions in which the semiconductor is dissolved into a liquid.

In the case of an inert solvent (which does not interact with the semiconductor) the activation energy of the dissolution reaction can be calculated from the linearity relationship

$$H_{\text{к}}^{\neq} = H_{\text{g}}^{\neq} - \alpha\Delta H_{solv} , \qquad (15)$$

where $H_{\text{K}}^{\neq}$ and $H_{\text{g}}^{\neq}$ are the activation energies of the reaction in the condensed and in the gas phase respectively, ΔH_{solv} is the enthalpy of solvation of the reaction product, and α is a fractional coefficient determined by the shapes of the potential surfaces. If the reaction product is chosen as the inert solvent the heat of solvation is equal to the heat of evaporation of the solvent. An example of this type of reaction is the interaction between germanium and a solution of bromine in $GeBr_4$.[20,21] In this case the activation energy of the reaction between germanium and bromine in a condensed phase is 25 kcal mole^{-1}, i.e. it is lower than the activation energy for the same reaction in the gas phase (33 kcal mole^{-1}) by an amount equal to the heat of evaporation of $GeBr_4$ (9 kcal mole^{-1}). It follows that $\alpha = 1$, and that the intermediate complex (in the case of an activated reaction) is relatively long-lived.

The value $\alpha = 1$ is typical of barrierless reactions[23], but since in this case the activation energy is high we cannot observe this behaviour experimentally in low-boiling liquids. However, suitable conditions may be met in the thermal oxidation of semiconductors, which we shall discuss below.

Clearly, in order to interpret the dissolution of semiconductors in polar liquids we need to know the composition of the reaction products and their heat of solvation. In many systems of great practical importance these characteristics are not known. In the absence of satisfactory methods of numerical estimation we must rely on expressions for the dependence of the kinetic characteristics of a reaction on the composition and properties of the solvent. This approach is discussed in detail in Ref.8.

VII. INITIAL STAGES OF OXIDATION

We shall use the considerations outlined above to discuss the special features of the thermal oxidation of semiconductors. At first sight the kinetics and mechanism of the reaction of silicon (say) with bromine and with oxygen have very little in common, since the former produces the volatile $SiBr_4$ whereas the latter produces a layer of SiO_2 whose thickness is determined by the rate at which oxygen can diffuse through it. We should immediately point out that when discussing the kinetics and mechanism of reactions at a phase boundary, i.e. of thermal oxidation processes, we are concerned with changes in instantaneous reaction rates, which can be determined experimentally by extrapolating to zero time the differential with respect to time of the thickness of the initial oxide layer. In this sense it is preferable to rely on experimental data obtained at moderately high temperatures or for relatively thin oxide layers.

The first step in our discussion is to examine the adsorption processes taking place during the initial stages of oxidation, and to establish the criteria which govern the transition from dissolution of the semiconductor in the gas phase (etching) to dissolution into an oxide phase (oxidation). We shall consider the steady-state reaction at constant temperature T and oxidiser pressure p in the gas phase. Using the symbol k_1 for the rate constant of the adsorption of the oxidiser on the atomically clean semiconductor surface we can express the rate of adsorption as

$$w_{\text{ads}} = k_1 p(1-\theta) .$$

The coverage of the surface (θ) by particles of oxidiser is given by the sum $\theta_1 + \theta_2$, where the first term defines the fractional monolayer coverage of the surface by irreversibly chemisorbed oxidiser, while the second term describes the surface coverage by oxidiser species in the second and higher adsorption layers. In the latter case the adsorption is treated as reversible, and is characterised by the equilibrium constant a and by the relatively low heat of adsorption q_2. Under these conditions

$$\theta_2/\theta_1 = ap/(1+ap) . \qquad (16)$$

The adsorption processes are accompanied by the transfer of semiconductor atoms to the gas phase with a rate constant $k_{2\text{g}}$ and to the oxide phase with a rate constant $k_{2\text{K}}$. The condition for the transition from dissolution into the gas phase to the formation of an oxide layer is the equality of the rates w_1 and w_2, i.e.

$$k_{2\text{g}}\theta_1 = k_{2\text{к}}\theta_2 , \qquad (17)$$

corresponding to

$$k_{2\text{g}}/k_{2\text{к}} = ap_{\text{кр}}/(1+ap_{\text{кр}}) . \qquad (18)$$

We shall assume that for a barrierless surface reaction the activation energy of the reaction with rate constant $k_{2\text{K}}$ is lower by ΔH_{solv} than the activation energy of the reaction with rate constant $k_{2\text{g}}$ [Eqn.(15)]. Thus, since

$$\exp(\Delta H_{solv}/RT) \ll 1,$$

we have

$$p_{\text{кр}} = a_{02}^{-1}\exp\left(\frac{\Delta H_{solv} - q_2}{RT}\right) . \qquad (19)$$

It follows from this expression that the condition $p < p_{\text{Kp}}$ corresponds to the formation of a gaseous product (i.e. to etching of the semiconductor), whereas the condition $p > p_{\text{Kp}}$ corresponds to oxidation with formation of a layer of oxide phase. Evidently, by plotting $\lg p$ against $1/T$ we obtain a straight line which divides the pressure–temperature space into two regions corresponding to etching and to oxidation respectively. The slope of this straight line is determined by the quantity ($\Delta H_{\text{solv}} - q_2$). The parameter q_2 can be identified with the heat of dissolution of the oxidiser in the oxide phase. In many systems (for example, in the SiO_2 system) this parameter is of the order of 1 kcal mole^{-1},[7] and therefore it lies within the uncertainty limits of ΔH_{solv}, which thus plays the main role in determining the condition (19). The coefficient a_{02} can be estimated by model calculations, and is typically in the range 10^{-3}–10^{-4} Torr^{-1}.[14,15] Some values of ΔH_{solv} are calculated below, and used (see Table) to compare calculation with experiment for the oxidation of silicon[30,31] and the sulphidation of germanium[14]. Calculations by Eqn.(19) agree in order of magnitude with experimental data on the sulphidation of germanium at 461 °C. For the oxidation of silicon the limiting oxygen pressure (above which an oxide layer begins to be formed) is 1×10^{-2}

Torr at 1100 °C, as compared with an experimental value[31] of 4×10^{-2}–1×10^{-1} Torr. For higher oxidation temperatures the calculated values are an order of magnitude lower than the experimental values. However, we should note that the conditions used in those experiments[30,31] may have produced rate limitation by diffusion of the reactants in the gas phase.

Thermodynamic and kinetic characteristics of germanium and silicon oxidation reactions (kcal mole^{-1}).

U	A_2	Bond Strength			$\frac{1}{2}H_{ads}(A_2)$	ΔH^{form}_{298} (UA)	$H^{\neq}_{2g}$	ΔH_{solv}	$H^{\neq}_{2K}$
		U–U	U–A	U=A					
Ge	S_2	44.5 [65]	68 [3]	131 [61,65]	24 [6]	23.5 [61]	43.0 [14]	−7	36
Ge	O_2	44.5 [65]	85	156 [61,65]	70 [49]	−7.7 [61]	57 [16]	−14	41
Si	O_2	53.5 [65]	111 [34]	190 [65]	110 [49]	−26.7 [66]	83 [62]	−32	52

VIII. KINETIC CHARACTERISTICS OF REACTIONS AT THE SEMICONDUCTOR–OXIDE PHASE BOUNDARY

A large volume of experimental information on the thermal oxidation of silicon is now available. The following results are especially relevant to our discussion.

1. Beyond a certain thickness, the oxidation of silicon is controlled by the rate of diffusion of oxygen to the semiconductor–oxide interface. It has been shown that the oxygen diffuses as undissociated particles: O_2 molecules or O_2^- molecular ions[7,32–35]. The reaction rate is usually proportional to the oxygen pressure.

2. The presence of SiO_x structural units at the semiconductor–dielectric interface, where $x < 2$, has been confirmed by electron spectroscopy methods. At the Si–SiO_2 interface the thickness of the intermediate layer is 2–10 Å, but unusual properties are observed up to oxide thicknesses of 100–150 Å.[36–44]

The thermal oxidation reaction of germanium has been studied in detail for the germanium–sulphur system[14]. It was shown that the diffusion of sulphur through a layer of germanium disulphide up to 1 μm thick does not limit the rate of sulphidation. The intermediate layer is 100–200 Å thick and its thickness depends on the total thickness of the sulphide layer.

3. The layer of silicon dioxide is in a glassy state whose structure is described by two levels of ordering: short-range order, determined by the presence of tetrahedral $SiO_{4/2}$ structure units, and the ordering associated with various arrangements of the initial structure units to give ring and spiral structures which form microscopic pores and extensive channels along which the oxygen species can diffuse[45–48].

These observations allow us to describe the kinetic model of the thermal oxidation reaction of silicon at the semiconductor–dielectric interface as follows. The region close to the interface (Fig. 2) includes a layer of oxide (to the right of the geometric boundary) containing randomly distributed microscopic holes which are arbitrarily shown as spheres. Some of these holes are occupied by oxidised (A_2) molecules whose state can be defined as free gas-phase particles in a volume of linear dimension d. The transition of an A_2 particle from an occupied to an empty hole and back is described by the rate constants k_1 and k_{-1}. A special situation arises when the hole is directly adjacent to the geometric boundary. An A_2 particle entering such a hole can undergo a non-activated interaction with an atom of the semiconductor at the crystal surface (U), and the rate constant of the step leading to the formation of the intermediate compound $\geq$U=A is k_2. We shall assume that in this step the characteristics of the chemical interaction of the oxidiser particle with the atom from the crystal are the same for dissolution into the gas and for the formation of an oxide phase. The process is completed by the incorporation of the intermediate compound UA into the network of structure units of the oxide, characterised by the rate constants k_3 and k_{-3}. The energetics of this step (ΔH_{solv}) define the solvation of the UA species.

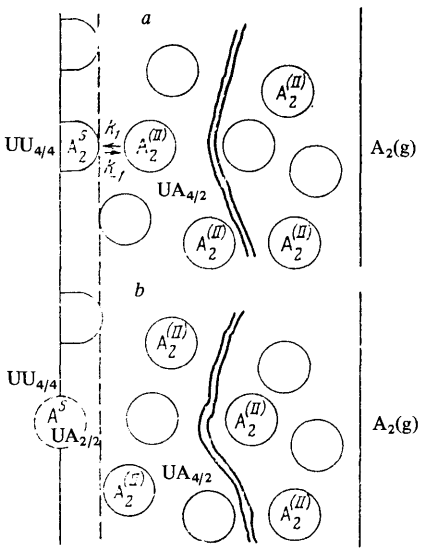


Figure 2. Schematic model of the thermal oxidation of a semiconductor U by interaction with A_2 to give a layer of $UA_{4/2}$: (*a*) adsorption of A_2 with rate constant k_1, (*b*) formation of the intermediate oxidation product $UA_2/_2$ with rate constant k_2. Microscopic holes in the oxide layer are shown. The concentration of $A_2^{(II)}$ is constant throughout the thickness of the layer. The broken line indicates the intermediate (translational) layer at the U–UA_2 boundary.

The sequence of steps involved in the oxidation of silicon by oxygen can be described as follows[49–56]. The initial step is the chemisorption of oxygen molecules with formation of an adsorbed intermediate on a surface centre, which we assume to be a doubly coordinated silicon atom, $\geq$Si, corresponding (strictly speaking) to a (100) orientation of the crystal:

$$\geq Si + O_2 \rightarrow \geq Si \cdot O_2 \text{ (chemisor.)}$$

The second step leads to an oxidative form of adsorption:

$$\geq Si \cdot O_2 \text{ (chemisor.)} \rightarrow \geq Si{=}O + O \text{ (ads.)}$$

This results in the dissociation of an O_2 molecule in the adsorption layer, one of the oxygen atoms becoming incorporated in the surface centre by a double bond. The other oxygen atom is held by an adsorption bond whose form is not clearly understood. We should stress that in the case of the reaction at the silicon–silica interface the probability of finding two adjacent surface centres (each capable of forming an $\geq$Si=O structure) is very low. In this case the second oxygen atom probably forms a metastable adsorption bond with atoms of the glass network: for example, giving an

Si–O–O–Si peroxide group. The last step limits the rate of the overall process and controls the removal of silicon atoms from the crystal and their incorporation into the network of silicon dioxide:

$$\rangle \mathrm{Si{=}O} \rightarrow \mathrm{SiO}_{2/2} \ . \qquad (20)$$

The oxidation process is completed by the formation of an $SiO_4/_2$ structure unit:

$$\mathrm{SiO}_{2/2} + \mathrm{O\,(ads.)} \rightarrow \mathrm{SiO}_{4/2} \ . \qquad (21)$$

Thus our model is generally consistent with the sequence of steps (1)–(3) proposed above, and the general kinetic equation for the rate of the thermal oxidation process can be written in the form of Eqn.(4). Since the solubility of A_2 particles in the oxide is usually low, i.e. $(k_1/k_{-1})[A_2] \ll 1$, and in most cases $[A_2] = \kappa p_{A_2}$ (where κ is the Henry coefficient and p_{A_2} is the partial pressure of A_2 particles in the gas), we can write

$$w_2 = k_2 k_1 \kappa p_{A_2}/(k_2 + k_{-1}) \ . \qquad (22)$$

There are two important special cases. At relatively low temperatures, when $k_2 \ll k_{-1}$, Eqn.(22) simplifies to

$$w_2 = k_2 k_1 \kappa p_{A_2}/k_{-1} \ . \qquad (23)$$

On the other hand at high temperatures ($k_2 \gg k_{-1}$) we have

$$w_2 = k_1 \kappa p_{A_2} \ . \qquad (24)$$

These two cases correspond to rate limitation at the semiconductor–oxide interface [Eqn.(23)] and to slow supply of A_2 particles to the interface [Eqn.(24)] respectively. In the latter case p_{A_2} is the equilibrium pressure, determined by the concentration of oxidiser dissolved in the layer adjacent to the semiconductor–oxide interface.

IX. COMPARISON WITH EXPERIMENT

The main characteristics of the dissolution of O_2 in silicon dioxide have been discussed by various workers[24,57–59]. The heat of dissolution is found to be ~0.7 kcal mole^{-1}, and the Henry coefficient is $\kappa = 0.0017$ at 900 °C. It has also been shown[34,35,58] that the rates of oxidation of silicon (in the parabolic regime) and of penetration of O_2 through the SiO_2 are almost identical, so that in our symbols the rate constant can be expressed as

$$k_1, \mathrm{cm^2\ s^{-1}} = 2.8 \cdot 10^{-4} \exp\,(-27.6/RT) \ . \qquad (25)$$

In Eqn.(23) the ratio k_1/k_{-1} is the constant for the adsorption equilibrium

$$a^{\kappa} = \frac{k_1^0}{k_{-1}^0} \exp(q_2/RT).$$

We shall assume that the heat of adsorption of O_2 at the $Si–SiO_2$ interface is equal to the heat of adsorption of oxygen for coverages greater than a monolayer.

Then, using Eqn.(8) with $d = 4$ Å, we can calculate the pre-exponential factor C_T of Eqn.(23):

$$C_T = \frac{kT}{h} n_s a_{O\kappa} \ . \qquad (26)$$

In this expression k is Boltzmann's constant h is Planck's constant, T is the absolute temperature, n_s is the concentration of active sites on the silicon surface, corresponding to the average density of holes at the geometric boundary which are filled with oxygen molecules, and $a_{OK} \cong 10^{-2}$ cm^3 mole^{-1}. The solubility of O_2 in silicon dioxide is typically[34,36,37] 5×10^{16} cm^{-3}, or 1.5×10^{11} cm^{-2}, so that we obtain $C_T = 9 \times 10^{21}$ atoms cm^{-2} s^{-1} from Eqns.(23) and (26). This value is close to that obtained from van der Meulen's results[60] (7.6×10^{22} atoms cm^{-2} s^{-1}).

The activation energy for the case described by Eqn.(23) can be calculated by the expression

$$H_{2\kappa}^{\neq} = H_{2g}^{\neq} - \Delta H_{solv} - q_2 \ , \qquad (27)$$

where $H_{2g}^{\neq}$ is the activation energy for the formation of the gas-phase molecule (in this case SiO).

In contrast to the dissolution of semiconductors in electrolyte solutions or in molecular liquids, in the case of thermal oxidation the use of the solvation energy concept requires some clarification. By definition, the solvation energy is the energy evolved when a particle is transferred from a vacuum to the stated medium. If the dissolution product is chemically identical to the medium this quantity is equivalent to the heat of evaporation or sublimation. In many polar or molecular solutions the molecular relaxation time of the medium is so short that the activated complex (or intermediate compound) produced during the dissolution reaction can be assumed to be fully solvated, and the activation energy of the reaction can be calculated by using Eqn.(15). However, in the thermal oxidation of semiconductors the rate of structural relaxation is comparable to the rate of chemical reaction at the phase boundary, which formally implies that the intermediate product of the reaction is only partially solvated. This aspect of the reaction is accounted for by the scheme suggested above for the oxidation of silicon.

Whereas the silicon atoms in the bulk of the oxide have a four-fold coordination, the intermediate compound formed during the rate-limiting step has only two-fold coordination. This is a feature of all the thermal oxidation reaction of semiconductors. Since the nearest neighbour approximation is very accurate in covalently bonded systems, the solvation energy of the intermediates in these reactions can be calculated. It is easy to show that the parameter of interest (ΔH_{solv}) is given by

$$\Delta H_{solv} = H_{U=O} - 2H_{U-O}, \qquad (28)$$

where $H_{U=O}$ is the energy of the double bond in the U=O molecule (for example, SiO), and H_{U-O} is the energy of the U–O single bond (for example, Si–O). By using data for the germanium–sulphur[3,61], germanium–oxygen[3,61], and silicon–oxygen[34] systems we obtained the ΔH_{solv} values given in the Table. We note that the solvation energies are highest for the silicon–oxygen system. The qualitative conclusion from this observation is that in the silicon–oxygen system the semiconductor atoms can be most effectively incorporated into the network of the glassy dielectric layer. By combining these results with experimental values of the activation energy for the dissolution of semiconductors in the appropriate gases[14,16,17,62] we can calculate [by Eqn.(27)] the activation energies for the thermal oxidation ($H_2^{\neq}$) of the semiconductors, which are also given in the Table.

For the germanium–sulphur system comparison with experiment is possible by using the results of Ref.14. The comparison shows that the contribution from the entropy of activation is often important in interfacial reactions, and cannot be ignored. As we have shown[14], the entropic contribution to the activation of the surface complex includes cooperative effects in the layer of sulphide adjacent to the crystal. It is difficult to allow for these effects with adequate precision, but it can be shown that the free energy of activation of the sulphidation reaction corresponds (to within ±8 kcal mole^{-1}) to the activation energy for the dissolution of germanium in sulphur vapour. Since ΔH_{solv} for this system is 7 kcal mole^{-1}, the conclusion is confirmed.

For the germanium–oxygen system the tabulated value is a first estimate of the activation energy of the oxidation process, determined by the reaction at the phase boundary.

For the thermal oxidation of silicon the activation energy of the initial stages was found[60] to be 53.7 kcal mole^{-1}, and an activation energy of 60 kcal mole^{-1} was reported[63] for the region 750–900 °C. These experiments were carried out under conditions favouring rate limitation by the reaction at the interface. The published values of the activation energy are not inconsistent with our estimate of 52 kcal mole^{-1}.

The solvation of the reaction product can be discussed by using a model of the reactive centre consisting of one structure unit of the crystal and one structure unit of the dielectric. This model is obviously valid at temperatures below the glass transition temperature T_g. Above T_g the kinetic processes associated with the switching of valence bonds are strongly hindered, and the activation volume often includes several dozen structural units[64]. As a result, heats of solvation calculated by Eqn.(28) can be expected to be inaccurate.

However, at temperatures above T_g the reactions may take place not through the formation of the intermediate complex $UO_{2/2}$ but directly by the breaking of a U–U bond in the activated complex $U_{2/4}UO$, giving a $UO_{4/2}$ structure unit. This means that the heat of solvation increases almost two-fold, and the activation energy of the reaction at the phase boundary is correspondingly reduced. This effect may explain the decrease in the activation energy of the oxidation from 60 kcal mole^{-1} (at 750–950 °C) to 26.8 kcal mole^{-1} (above 950 °C).[63] Unfortunately the glass transition temperature is not always accurately known. For quartz glass $T_g \cong$ 1157 °C,[34] but there are reasons to believe that very thin layers may soften at a lower temperature. We should re-state the need to allow for the entropic contribution to the activation of the surface complex when the oxidation reaction takes place under conditions compatible with viscous flow of the glassy oxide[9,13,14].

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Our analysis of experimental data on the kinetics of the dissolution and of the thermal oxidation of semiconductors has shown that these two reactions have the same elementary step whose nature is determined by the activated displacement of a surface atom. This allows us to calculate the kinetic characteristics of the process at the semiconductor–oxide interface during thermal oxidation if the characteristics of the dissolution of the semiconductor into the gas phase and of the solvation of the intermediate by the oxide layer are known. In covalent systems the heats of solvation can be calculated by the two-fold coordination model of the semiconductor atom in the nearest neighbour approximation. The structure-chemical theory of reaction kinetics on a semiconductor surface and of relaxation processes in glass oxides offers a unified approach to the semiconductor oxidation reactions. As a result, an atomic–molecular theory of semiconductor–dielectric systems can be developed and used to synthesise materials having prescribed properties.

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Reactions of Hydroperoxides with Amines and Aminoalcohols in Aqueous Solutions in the Presence and Absence of Metal Ions

S.K.Grigoryan

The intermolecular interactions in hydroperoxide-amine and hydroperoxide-amine-M^{2+} systems in aqueous media are examined. The formation of binary complexes between the system components is demonstrated; the amine complexes of metals $(MA)^{2+}$ show the highest activity in the decomposition of hydroperoxides. The fundamental kinetic characteristics of the decomposition reactions of hydroperoxides with amines in an aqueous medium in the presence and absence of metal ions are reduced from the data obtained and reaction mechanisms are proposed.
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I. INTRODUCTION

The study of the mechanism of the decomposition of hydroperoxides (ROOH) is of both theoretical and applied importance. They are intermediates in oxidation reactions in living organism and also in the autoxidation of low- and high-molecular weight organic substances. Hydroperoxy-compounds have found major practical applications as oxidising agents for various organic compounds and in the organic synthesis of oxygen, sulphur, phosphorus, and nitrogen compounds.

Nitrogen-containing organic compounds, particularly amines, aminoalcohols, aminoacids, etc. (present in the living organism as component parts of proteins and enzymes), form complexes with "metals of life" such as Co^{n+} (n = 2, 3), Cu^{n+} (n = 1, 2), Fe^{n+} (n = 2, 3), Mo^{n+} (n = 5, 6), Mn^{n+} (n = 2, 3, 4), Na^+, K^+, Zn^{2+}, Mg^{2+}, Ca^{2+}, etc. Some of them induce the catalytic decomposition of hydroperoxides in aqueous solutions analogous to that observed in enzyme catalysis.

The oxidation of high-molecular-weight compounds (polymers, rubbers, etc.) is an undesirable phenomenon which leads to their degradation and ageing. (Oxidation with atmospheric oxygen results in the formation on the hydrocarbon chains of the polymer of hydroperoxy-groups OOH, whose radical decomposition actually induces the degradation and hence also the ageing of polymers.) The elimination of or the prevention of the formation of the ROOH groups in macromolecules can be achieved by employing certain aminoalcohols and amine complexes as stabilisers.

This review deals with the kinetics and mechanisms of the reactions of cumenyl or t-butyl hydroperoxides with amines (A) in the presence and absence of M^{2+} ions in aqueous solutions. The studies were undertaken to elucidate the mechanism of the decomposition of hydroperoxides in aqueous media, to select amino-compounds and their complexes for reactions with specified pathways and products, and to select the necessary systems consisting of amines and M^{2+} complexes to be used as stabilisers in adhesive latexes and rubbers based on polychloroprene. In addition, the results obtained in studies on ROOH–A and ROOH–A–M^{2+} systems made it possible to explain the positive influence of Cu^{2+}, Co^{2+}, and monoethanolamine on the organisms of animals and man.

The kinetics of the formation and decomposition of ROOH in the absence and presence of variable-valence metal ions in organic solvents have been studied[1–7]. This review deals with investigations in aqueous media. All vital processes occur in water and nitrogen-containing compounds and hydroperoxides play an important role in them[8].

II. INTERMOLECULAR INTERACTIONS IN HYDROPEROXIDE–AMINE AND HYDROPEROXIDE–AMINE–M^{2+} SYSTEMS IN AQUEOUS MEDIA

The H_2O–ROOH–A–M^{2+} system is complex and several processes and reactions can occur simultaneously in it. In order to elucidate the character and mechanisms of the possible individual stages, studies were therefore made of complex formation and the binary interactions between the system components.

1. Complexes between ROOH and A

De La Mare et al.[9] showed in an earlier study that the interaction of hydroperoxides with amines in solution in the latter results in the formation of a hydrogen-bonded complex;

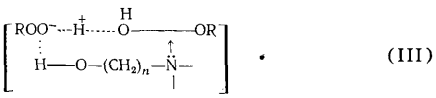
$$[ROO{-}H \leftarrow \ldots : \underset{|}{N}{-}] \quad . \qquad (I)$$

It has been shown[10,11] that the interaction of a hydroperoxide with amines in aqueous media involves conjugation between the electrons at the nitrogen atom and the oxygen bond with formation of a complex having a different structure:

$$\left[\begin{array}{c} \\ -\underset{|}{N}- \\ \vdots \\ RO\text{———}OH \end{array}\right] . \qquad (II)$$

The formation of complex (II) in aqueous media had been postulated earlier on the basis of kinetic data[12]. The authors of that investigation[12] also suggested that complex (III) between the ROOH dimer and an aminoalcohol molecule is

formed, in addition to complex (II), in aqueous solutions in the presence of aminoalcohols:

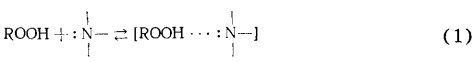


(III)

Subsequently this was also demonstrated by infrared spectroscopy[13].

It has been shown by NMR that complexes are formed in organic solvents (benzene, acetone, ethanol, etc.). The chemical shifts of the OOH group in t-butyl (TBHP), cumenyl (CHP), and t-pentyl hydroperoxides on formation of complexes with proton-accepting compounds (ethers and amines) have been investigated[14,15]. Depending on the concentration of, for example, triethylamine (TEA), there are three types of associated species (i.e. hydrogen-bonded complexes between TEA and TBHP) with a 1 : 1 composition; the hydroperoxide–hydroperoxide complex of the type ROOH....OOR predominates at low amine concentrations, while at high amine concentrations a complex resembling (II) is the dominant species. According to Yablonskii and co-workers[14,15], the O–O bond of the hydroperoxide in the complexes with amines is weakened more than in associated species with other proton acceptors and for this reason ROOH in saturated hydrocarbons (at 130–140 °C) and in water (up to 90 °C) are thermally stable[12,16], while in the presence of amines in aqueous solutions they decompose already at 30–40 °C.[12] Since the O–O bond of the hydroperoxide in complex (II) is weakened, the reaction is of first order with respect to ROOH.[12]

The formation of complexes between CHP and TEA has been investigated by proton magnetic resonance (^{1}H NMR) in aqueous solution at 34 °C.[17] It was found that the complex has the 1 : 1 composition and that the equilibrium



(1)

exists. The complex formation constant (K_p = 0.18 litre mol^{-1} at 34 °C) was calculated graphically[18] using the equation

$$\Delta/[A]_0 + K_p\Delta = K_p\Delta_0 \qquad (2)$$

where Δ_0 is a standard quantity which represents the difference between the chemical shifts of the OOH group in the complex and in the ROOH–cyclohexane system (CHP was diluted with an inert solvent—cyclohexane), Δ is the difference between the chemical shifts of the CHP–TEA system in cyclohexane and of the CHP–cyclohexane system and is a measure of the reaction between OH and  alone, and $[A]_0$ is the initial amine concentration; we have $[A]_0 \gg [ROOH]$.

2. Complex Formation Reactions between A and M^{n+}

The thermodynamically stable ammine and amine complexes of copper and cobalt have the composition $(MA_4)^{2+}$.[19] Kinetic studies have shown that the decomposition of the hydroperoxide in the presence of M^{n+} complexes of amines obeys a first-order equation with respect to the amine[20,21]. Spectroscopic measurements (infrared spectroscopy and NMR) also indicate the formation of complexes in aqueous media between amino-compounds and metal ions[19,22]. It follows from the data of Grigoryan and co-workers[21,23] that 1 : 1, 1 : 2, and 1 : 3 complexes are formed together with the complexes $(MA_4)^{2+}$ in aqueous solutions of monoethanolamine, TEA, morpholine, etc. in the presence of Cu^{2+} and Co^{2+}.

The formation of complexes between ligands and M^{2+} was demonstrated by ^{1}H NMR [24,25] on the basis of the paramagnetic shifts of the M^{2+} signals in the presence of different ligands. The NMR spectra of the coordinated ligands not only yield information about the delocalisation of spin density over the bond system of the ligand but also make it possible to determine the equilibrium (complex formation) constant, the heat of complex formation, and other parameters[26].

The concentration dependence of the ^{1}H NMR spectra of TEA (taken in excess) in the presence of Ni^{2+} in aqueous solutions has been investigated[23]. The magnitude and signs of the spin density of the protons in the TEA molecules as well as the constant for the complex formation reaction between TEA and Ni^{2+} were determined from the shifts of the signals; the complex has the 1 : 1 composition. A downfield shift of the signals of the protons in the methylene and methyl groups of TEA was observed in the test solutions, for $[TEA]_0$ = 0.05–0.35 M and $[Ni^{2+}]_0 = 5 \times 10^{-3}$ M, the shift of the methylene proton signals being greater than the shift of the methyl proton signal. At the same time the multiplet signals of these groups are broadened and distorted, which indicates the existence in the solutions of labile paramagnetic complexes[27]. The signals for the CH_2 and CH_3 group are displaced downfield, which means that positive spin density is located on the protons of these groups following the formation of complexes. The dependence of the shift of the NMR lines on the ligand concentration is described by the formula[28,29]

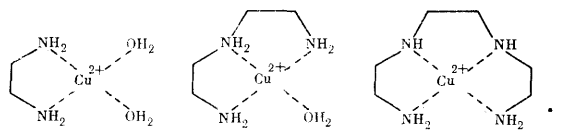
$$-\mu/\delta = 1/\alpha aK + S/\alpha a\,, \qquad (3)$$

where μ is the molar concentration of the paramagnetic substance (in this case Ni^{2+}), δ the paramagnetic shift (p.p.m.) equal to the difference between the chemical shifts in the presence and absence of paramagnetic species (Ni^{2+}), S the molar concentration of TEA with $[TEA]_0 \gg [Ni^{2+}]_0$, K the complex formation constant, a the hyperfine coupling (HFC) constant (G) at 304 K, and α = 72.8). The HFC constants for the methylene and methyl protons of TEA and the complex formation constants were determined from the graphical analysis of the linear dependence of μ/δ on $[TEA]_0$ and $a^H_{CH_2}$ = +0.02 G, $a^H_{CH_3}$ = +0.008 G, and $K = 1.32 \times 10^2$ litre mol^{-1} (34 °C) were obtained.

The mechanism of the transfer of spin density to the atomic orbitals of the TEA molecule is as follows. For chelate Ni^{2+} complexes of amines, the unpaired electron is delocalised as a result of the formation of a σ-bond. The unshared electron pair of the nitrogen atom and the d_{z^2} orbital of the Ni^{2+} ion are involved in the formation of the Ni^{2+}–TEA σ-bond. In this case the spin density at the nitrogen atom is positive.

On comparing the complex formation constants obtained for Ni^{2+} ($K = 1.32 \times 10^2$) with the constants for the analogous Co^{2+} ($K = 2.6 \times 10^4$) and Cu^{2+} ($K = 6.1 \times 10^{15}$) complexes[30,31], we may note that the Ni.TEA complex is less stable. It is noteworthy that, in contrast to the analogous Cu^{2+}, Co^{2+}, and Mn^{2+} complexes, the above complex does not exhibit catalytic activity in the CHP and TBHP decomposition reactions in an aqueous medium[21]. The presence of free orbitals in the chelate complex apparently also plays an important role under these conditions. Thus it has been found that the manifestation of a catalytic activity by chelate Cu^{2+} complexes of diamines requires that the complexes contain two coordination-unsaturated bonds. The chelate Cu^{2+} complexes in which all the orbitals are occupied are inactive in the ROOH or HOOH decomposition reactions[32]. This is evident from a

comparison of the chelate copper(II) complexes of the following diamines: ethylenediamine, diethylenediamine, and triethylenediamine; they are illustrated schematically below:



The activity in the ROOH or HOOH decomposition reactions decreases in the sequence ethylendiamine (en) ≫ diethylenediamine (dien) > triethylenediamine (trien), i.e. the complex in which the central atom is not fully blocked by the ligand proved to be the most active; complexes with tetradentate ligands show almost no catalytic activity.

3. The Formation of Complexes between ROOH and M^{n+}

The formation of an intermediate complex between the hydroperoxide and the metal ions in organic media has been established[33–36]. The formation of complexes between metal ions (Ni^{2+}, Mn^{2+}, etc.) and TBHP in CCl_4 and CH_2Cl_2 has been demonstrated by NMR.[29] The intermolecular interactions between ROOH and M^{n+} in aqueous solutions were first investigated by Markaryan et al.[37] At very high water concentrations it becomes almost impossible to demonstrate the occurrence of the interaction of ROOH with Mn^{2+}, since the signals of the hydroperoxide and water protons merge; the complex formation in the CHP–Co^{2+} system was therefore investigated at low water concentrations. The results made it possible to estimate quantitatively the degree of intermolecular interaction between the ROOH and M^{n+} in aqueous solutions. The concentration dependence of the shift of the signal due to the protons of the CHP molecule in aqueous solutions in the presence of an excess of the hydroperoxide (>97, 98, 98.5, and 99%) was investigated. The constant for the complex formation between CHP and Co^{2+} was determined by Eqn.(3) from the shift; it proved to be $K = 0.158$ litre mol^{-1} at 34 °C.

One must note that the interaction of the individual components (ROOH and A) with water (as the medium) was also investigated by ^1H NMR. After the addition of water to CHP, the signal of the OOH group of the hydroperoxide is slowly displaced downfield as a result of the formation of the hydrogen bond between ROOH and H_2O.[37] The calculated rate constants for proton exchange and the proton lifetime in the complex [ROOH...H_2O] formed are $K = 8.5 \times 10^{-1}$ s^{-1} and $\tau = 1.2 \times 10^{-2}$ s. The formation of associated species comprising water and the TBHP dimer under ambient conditions had been demonstrated previously by infrared spectroscopy[13]. It was also established[38,39] that associated species involving the amine and water are formed in aqueous solutions of amines via both hydrophobic and hydrophilic interactions.

Thus intermolecular interactions occur in aqueous ROOH + A + M^{n+} systems with formation of binary associated species and complexes differing in their stability. Under standard conditions, these intermediate compounds are stable (some of them exhibit a catalytic activity in the ROOH decomposition reaction). Among the binary complexes indicated, the highest activity is shown in the decomposition of cumenyl and t-butyl hydroperoxides in an aqueous medium by the complexes of the amine with the metal ions $(MA)^{n+}$; this is indicated not only by the formation constants but also by kinetic data obtained in the study of the decomposition of hydroperoxides under the influence of these complexes[17,20,21].

III. KINETICS OF THE REACTIONS OF HYDROPEROXIDES WITH AMINES AND AMINOALCOHOLS IN THE ABSENCE AND PRESENCE OF M^{2+}

1. Kinetics of the Decomposition of ROOH in the Presence of the Amine and M^{2+}

The complex formation constants for the components of binary systems are listed below[30,31]:

System	CHP-TEA	CHP-Co^{2+}	TEA-Ni^{2+}	MEA-Cu^{2+}
K_p, litre mol^{-1}	1.6	0.16	132	26 000

Their comparison shows that the complex $(MA)^{2+}$ should be the most active[17,23]. For example, the ratios $K_{A+M^{2+}}/K_{A+ROOH}$ and $K_{A+M^{2+}}/K_{ROOH+M^{2+}}$ are approximately 10^2–10^6. Indeed the kinetic data obtained confirm that the hydroperoxides in the H_2O–ROOH–A–M^{2+} systems decompose mainly catalytically[20,21] as a result of the effect of the complex $(MA)^{2+}$ (although two other reactions can also occur simultaneously with the above reaction), the rate of the reaction catalysed by the complex $(MA)^{2+}$ being several times that in the absence of the complex[20,21].

The data permit the following conclusions concerning the decomposition of ROOH in the presence of amines and metal ions.

1. In the presence of monoethanolamine, pyridine, and some of its derivatives at temperatures up to 80 °C hydroperoxides hardly decompose in aqueous media[40–42]. Nor do the ROOH decompose at an appreciable rate in the presence of only the cations Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, etc.) (up to 90 °C).[12,42,44]

2. The rate of decomposition of hydroperoxides in the presence of aminoalcohols and M^{n+} for $[A]_0 = [ROOH]_0$ in aqueous solutions is expressed by the general equation[40–44]

$$w_{tot} = -\frac{d[ROOH]}{dt} = w_1 + w_2 + w_3 = k_1[A]_0[ROOH]_0 + k_2[ROOH]_0^2 + k_3[M^{2+}]^n[A]_0[ROOH]_0 , \quad (4)$$

where w_1 is the initial rate of reaction directly between ROOH and the aminoalcohol, w_2 the initial rate of decomposition of the CHP dimer catalysed by the aminoalcohol, w_3 the initial rate of the catalytic reaction catalysed by the complex $(MA)^{2+}$, and n is the order of the reaction with respect to M^{2+}, which is between zero and 1.[21] The kinetics of the reaction of ROOH with aminoalcohols have been studied in the range 40–80 °C.[12] In the presence of aminoalcohols the amount of CHP in the system decreases as a result of the occurrence of two independent simultaneous reactions, both being of second order; although the aminoalcohol is involved in one of them, it is not consumed as a reactant: ROOH is consumed to a greater extent in the reactions with aminoalcohols than the aminoalcohol[12,42].

The excess consumption of the hydroperoxide is due to the occurrence of two simultaneous reactions, one of which takes place directly between the hydroperoxide and the aminoalcohol and the other involves the decomposition of the hydroperoxide by the aminoalcohol[12]. It has been established[40] that the first reaction, whose rate is w_1, takes place between ROOH and A molecules, while the second, whose rate is w_2, is the aminoalcohol-catalysed reaction between the $ROOH^-$ and $ROOH_2^+$ species, i.e. involves the formation of the cumenyl hydroperoxide dimer. Both reactions have a non-radical mechanism[40], although one cannot rule out a

slight "radical contribution" (3–5%) to the decomposition of the hydroperoxide in the presence of amines in aqueous solutions[52], despite the fact that this hydroperoxide decomposition pathway is difficult to demonstrate by a kinetic method. The catalytic activity of aminoalcohols (except monoethanolamine) can be explained by the presence of two groups in their molecules—proton donating (the hydroxy-group) and proton accepting (the nitrogen atom), which may entail the formation of complex (III).[12,40] Indeed in the presence of amines and without an alcoholic group hydroperoxides are not decomposed catalytically and only the direct reaction between ROOH and A takes place[41,45]. Table 1 shows that an increase in the number of hydroxy-groups and their removal from the nitrogen atom in the aminoalcohol molecule as well as the presence of hydrogen atoms at the nitrogen atom in the same molecule decrease the overall rate of decomposition of the hydroperoxide[12,40]: under these conditions, the formation of the intermediate active complexes (II) and (III) is hindered.

The replacement of the hydrogen atom in the alcoholic group by the methyl group deprives the amine of catalytic activity in the CHP decomposition reaction. It is thereby confirmed that the catalytic action of the aminoalcohol in the process under consideration involves the migration of the proton in the intermediate active complex (III).[12,41]

The presence of two idential proton-accepting centres (for example, in hydrazine $H_2\ddot{N}-\ddot{N}H_2$) does not lead to the catalytic decomposition of ROOH; the presence of pyridine or triethylamine together with ethanolamine in equimolar proportions or separately does not induce the catalytic decomposition of CHP.[12,41] The catalytic decomposition of the hydroperoxide requires the joint presence in the same molecule of two opposed active centres[12,40,41].

At 30° and 35 °C and for $[CHP]_0 = [TEA]_0$, the consumption of the aminoalcohol is not observed, whereas more than 10% of the initial amount of the hydroperoxide is consumed. i.e. only the catalytic decomposition of ROOH takes place[12]. In addition it has been shown kinetically that a little less than 10% of the consumption of the hydroperoxide is due to its decomposition purely via the catalytic pathway (the overall ratio of the consumptions of ROOH and A is 1.12 : 1). A similar equimolar amount of oxygen evolved was determined in the overall ROOH decomposition reaction in the presence of triethanolamine under the same conditions[12,40].

Table 1 presents kinetic data for the reaction of CHP with amines in an aqueous medium at 80 °C [k_1 and k_2 are the rate constants for the first and second reactions catalysed by the aminoalcohol (litre mol^{-1} min^{-1}); $k = k_1 + k_2$; for amines without alcoholic groups, $k_2 = 0$]. For comparison, Table 1 also lists the activation energies E (kcal mol^{-1}) and pre-exponential factors A (litre mol^{-1} min^{-1}) for the first and second reactions.

Thus, in the presence of only aminoalcohols such as diethanolamine, triethanolamine, diethylaminoethanol, diethylaminopentanol, diethylbutanolamine, diethyl-2,3-dimethylaminopropanol, β-piperidinylethanolamine, etc. (except monoethanolamine), the rate of reaction is expressed by the following equation[21,40]:

$$w_{tot} = w_1 + w_2 = k_1[A]_0[ROOH]_0 + k_2[ROOH]_0^2 \qquad (5)$$

if $[A]_0 = [ROOH]_0$. If has been shown[40] that w_1 and w_2 are comparable in magnitude; for example, $w_1/w_2 = k_1/k_2 = 1.67$ for the reaction of CHP with triethanolamine at 80 °C.

It has been established by ^1H NMR [14,15,17] that at high amine concentrations a complex of type (II) predominates and there is therefore virtually no catalytic decomposition

Table 1. Kinetic parameters of the reactions of CHP with amines (in water at 80 °C).

No.	Amine	Formula	k, litre mol^{-1} min^{-1}	k_1, litre mol^{-1} min^{-1}	k_2, litre mol^{-1} min^{-1}	E_1, kcal mol^{-1}	E_2, kcal mol^{-1}	$10^{-8}A_1$, litre mol^{-1} min^{-1}	$10^{-8}A_2$, litre mol^{-1} min^{-1}
1	Monoethanolamine	$H_2N-CH_2-CH_2-OH$	0	0	0	—	—	—	—
2	Diethanolamine	$HN-(CH_2-CH_2-OH)_2$	0.124	0.040	0.084	20.6	17.7	2880	28.5
3	Triethanolamine	$N-(CH_2-CH_2-OH)_3$	0.165	0.100	0.065	13.7	19.7	0.0484	167
4	Diethylaminoethanol	$(C_2H_5)_2-N-CH_2-CH_2-OH$	0.584	0.480	0.104	17.8	17.8	537	155
5	Diethylaminopentanol	$(C_2H_5)_2-N-(CH_2)_5-OH$	0.720	0.658	0.062	*	—	—	
6	Diethylaminobutanol	$(C_2H_5)_2-N-(CH_2)_4-OH$	0.570	0.468	0.102	*	—	—	—
7	Dimethylaminoethanol	$(CH_3)_2-N-CH_2-CH_2-OH$	0.479	0.380	0.099	*	—	—	—
8	Diethylisobutanolamine	$(C_2H_5)_2-N-CH_2-\underset{\displaystyle OH}{\underset{\vert}{CH}}-CH_2-CH_3$	0.592	0.500	0.092	*	—	—	—
9	Diethyl-2,3,-diethyl-aminopropanol	$(C_2H_5)_2-N-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-OH$	0.303	0.230	0.078	*	—	—	—
10	Triethylamine	$N-(C_2H_5)_3$	0.171	0.171	0	14.7	—	5.4	—
11	Diethylamine	$HN-(C_2H_5)_2$	0.192	0.192	0	17.5	—	87.1	—
12	Piperidine	$H_2C\begin{cases}CH_2-CH_2\\ CH_2-CH_2\end{cases}NH$	0.280	0.280	0	16.0	—	22.4	—
13	Pyridine	$HC\begin{cases}CH=CH\\ CH-CH\end{cases}N$	0	0	0	—	—	—	—
14	Morpholine	$O\begin{cases}CH_2-CH_2\\ CH_2-CH_2\end{cases}NH$	0.052	0.052	0	16.0	—	4.37	—
15	β-Piperidinylethanolamine	$H_2C\begin{cases}CH_2-CH_2\\ CH_2-CH_2\end{cases}N-CH_2-CH_2-OH$	0.287**	0.204**	0.083**	17.2	13.7	194	0.426
16	Methyl β-piperidinyl-ethyl ether	$H_2C\begin{cases}CH_2-CH_2\\ CH_2-CH_2\end{cases}N-CH_2-CH_2-O-CH_3$	0.338	0.338	0	16.5	—	44.8	—

*Values not determined.
**At 70 °C.

of the hydroperoxide under the influence of the aminoalcohol when $[A]_0 \gg [ROOH]_0$. For example, $w_1/w_2 = 15$ for the reaction of CHP with triethanolamine, i.e. the rate of the catalysed reaction may be neglected compared with w_1.[40] We therefore obtain from Eqn.(5)

$$w_{tot} = k_1[A]_0[ROOH]_0 . \quad (6)$$

In the presence of amines without alcoholic groups [triethylamine, diethylamine, morpholine, piperidine, methyl β-piperidinylethyl ether, octylmorpholine, hydrazine, etc. [except pyridine and its derivatives)] the rate of consumption of ROOH (in the absence of M^{2+}) is expressed by an equation[40,41,45] analogous to Eqn.(6):

$$w_{tot} = w_1 = k_1[A]_0[ROOH]_0 . \quad (7)$$

In the presence of M^{2+} for equal initial reactant concentrations, i.e. with $[A]_0 = [ROOH]_0$ it is necessary to use Eqn.(4) instead of Eqn.(5) whereupon the following expression is obtained:

$$w_{tot} = w_1 + w_3 = k_1[A]_0[ROOH]_0 + k_3[M^{2+}]^n[A]_0[ROOH]_0 . \quad (8)$$

The same expression is obtained from Eqn.(4) when $[A]_0 \gg [ROOH]_0$; as above, one can assume in this case that $w_2 \to 0$, since

$$w_2 \ll w_1 \text{ and } w_2 \ll w_3 .$$

When $[A]_0 \gg [ROOH]_0$ and in the case of monoethanolamine or pyridine for any amine concentration, only one reaction catalysed by the complex $(MA)^{2+}$ takes place, its rate being expressed by the equation

$$w_{tot} = w_3 = k_3[M^{2+}]^n[A]_0[ROOH]_0 = k_{cat}[ROOH]_0 , \quad (9)$$

where $k_3[M^{2+}]^n[A]_0 = k_{cat}$ (k_{cat} is a constant for given concentrations of M^{2+} and A).

Transformation of Eqn.(8) yields

$$w_{tot} = k_{non\text{-}cat}[ROOH]_0 + k_{cat}[ROOH]_0 = (k_{non\text{-}cat} + k_{cat})[ROOH]_0 = k_{eff}[ROOH]_0 , \quad (10)$$

where $k_{non\text{-}cat} = k_1[A]_0$. The constant k_{eff} is determined from Eqn.(10).

Table 2. Temperature variation of the rate constants for the decomposition of CHP and TBHP in the presence of the monoethanolamine–Cu^{2+} complex.

t, °C	$10^2 k_{CHP}$, min^{-1}	$10^2 k_{TBHP}$, min^{-1}
60	0.35	0.06
65	0.80	0.12
70	1.34	0.23
75	2.73	0.54
80	4.95	0.90

Note. The initial concentrations of monoethanolamine and ROOH were 0.05 M: $[CuSO_4]_0 = 10^{-3}$ M.

The rate constants for the decomposition of the hydroperoxide by the amine complex $(MA)^{2+}$ are calculated in this way. Next, taking into account the fact that $k_{non\text{-}cat}$ is known[40], k_{cat} is determined:

$$k_{cat} = k_{eff} - k_{non\text{-}cat} . \quad (11)$$

For monoethanolamine or pyridine, k_{cat} is determined from Eqn.(9). One must note that, in contrast to the direct interaction of ROOH with the aminoalcohol and the decomposition of the hydroperoxide dimer by the aminoalcohol[40,41], the catalytic ROOH decomposition reactions under the influence of the complex $(MA)^{2+}$ have a radical-chain mechanism, although the chains are very short[21]. In certain cases the radical character of the reaction is hardly noticed, as in the decomposition of CHP and TBHP in the presence of the 1 : 1 Co^{2+} or Cu^{2+} complex of monoethanolamine.

It is noteworthy that the rate of decomposition of CHP in the presence of the 1 : 1 Cu^{2+}–monoethanolamine complex exceeds severalfold the rate of decomposition of TBHP (Table 2).

Comparison of the temperature variations of the rates of decomposition of the above hydroperoxides readily shows that the rate of decomposition of CHP increases appreciably in the presence of the phenyl group in the hydroperoxide molecule (being a weaker electron donor than the methyl group, the phenyl group diminishes the electron density in the O–O bond and thereby facilitates the decomposition of the CHP compared with TBHP). The mechanism of the catalytic decomposition is apparently independent of the type of hydroperoxide, since the activation energies are almost identical:

$$k_{CHP}\,(min^{-1}) = 8.13 \cdot 10^{17} \cdot \exp[(31\,000 \pm 500)/RT] \cdot$$
$$k_{TBHP}\,(min^{-1}) = 1.62 \cdot 10^{17} \cdot \exp[(31\,500 \pm 500)/RT] \cdot \quad (12)$$

Like metal ions, amines are catalysts of the decomposition of ROOH in aqueous solutions; it has been shown by the kinetic and chromatographic methods[21] that, in the course of the decomposition of ROOH, the amine is not consumed and after the complete decomposition of ROOH the amount of amine remains unchanged.

The rate of consumption of the hydroperoxide in the presence of Cu^{2+} is higher than in the presence of Co^{2+} or Mn^{2+}, which can be explained by the stability of the amine complexes whose criterion is the oxidation potential of the metal; there is a correlation between the normal oxidation potential of the cation and the rate of decomposition of the hydroperoxide: the rate of decomposition of ROOH increases in parallel with the increase of the normal oxidation potentials of M^{2+}.[21]

One must note that there are also other factors which influence the stability of metal ion complexes (the presence of unfilled orbitals in the complex, the charge and size of the ion, the nature or basicity of the ligand, and others[32]).

2. The Amine Complexes of Metal Ions as Models of Enzymes in the Decomposition Reactions of Cumenyl and t-Butyl Hydroperoxides in an Aqueous Medium

The hypothesis of the formation of an intermediate active complex of the type $[ROOH...(MA)^{2+}]$ has been used to account for the kinetics of the homogeneous catalytic reactions of cumenyl and t-butyl hydroperoxides in the presence of an amine and M^{2+} in an aqueous medium[42].

As mentioned above, in the presence of amines or aminoalcohols and M^{2+} ions, the decomposition of the hydroperoxide catalysed by the M^{2+} complexes of the aminoalcohol may be accompanied by the simultaneous occurrence of other reactions. The complex catalyst (E), consisting of M^{2+} and A, can be regarded as the simplest analogue of an enzyme inducing the decomposition of hydroperoxides[42].

It is known[19] that the thermodynamically stable ammine or amine complexes of copper or cobalt have the composition $(MA_4)^{2+}$. Studies have shown[21] that the decomposition of ROOH obeys a first-order kinetic equation with respect to A, indicating that the amine complex of the bivalent metal involved in the chemical reaction has the composition $(MA)^{2+}$.

The formation of the given intermediate complex between the amine complex (E) and the hydroperoxide can be represented by the equation

$$E + n\text{ROOH} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [E \cdots n\text{ROOH}] \quad . \qquad (13)$$

Reaction (13) is reversible and, since $k_{-1} \gg k_1$, the equilibrium is established faster than the decomposition of the intermediate active complex[17,46]. All amines and aminoalcohols have the capacity to form such complexes in aqueous solutions[17,42], but MEA in the presence of Cu^{2+} or Co^{2+} constitutes a purely model system, because in the joint presence of the above reactants the catalytic process is not accompanied by other simultaneous reactions.

The equilibrium constant is given by

$$K = \frac{k_1}{k_{-1}} = \frac{[E \cdots n\text{ROOH}]}{[\text{ROOH}]^n [E]} \quad . \qquad (14)$$

If $[E]_0$ is the initial overall concentration of the bound and free catalyst, then the following relation is valid:

$$[E] = [E]_0 = [E \cdots n\text{ROOH}] \quad . \qquad (15)$$

On substituting Eqn.(15) in Eqn.(14), we obtain

$$K = \frac{[E \cdots n\text{ROOH}]}{[\text{ROOH}]^n ([E]_0 - [E \cdots n\text{ROOH}])} \quad ,$$

whence the concentration of the intermediate complex is given by the expression

$$[E \cdots n\text{ROOH}] = \frac{K [\text{ROOH}]^n [E]_0}{1 + K [\text{ROOH}]^n} \quad . \qquad (16)$$

The final reaction products are obtained as a result of the decomposition of this complex[21,46]:

$$[E \cdots n\text{ROOH}] \xrightarrow{k_{\text{decomp}}} (MA)^{2+} + \text{final products.} \qquad (17)$$

If the overall rate of decomposition of the initial hydroperoxide or the rate of formation of the reaction products are determined by the rate of reaction (17), one can write

$$w = d[\text{ROOH}]/dt = k_{\text{decomp}} [E \cdots n\text{ROOH}] . \qquad (18)$$

From Eqns.(16) and (18), we obtain an expression for w:

$$w = \frac{k_{\text{decomp}} K [\text{ROOH}]^n [E]_0}{1 + K [\text{ROOH}]^n} \quad . \qquad (19)$$

The initial concentration of the complex catalyst $[E]_0$ cannot be greater than the concentration of the metal ions (Cu^{2+}, Co^{2+}, Mn^{2+}, etc.). Consequently $[E]_0$ in Eqn.(19) can be expressed in terms of the initial concentration of the metal ion bearing in mind that the stability constants of the complexes $(MA)^{2+}$ are much greater than unity[17,30,31]. An equation of the Michaelis–Menten type is then obtained in the following form:

$$w = \frac{k_{\text{decomp}} K [\text{ROOH}]^n [M^{2+}]_0}{(1 + K [\text{ROOH}]^n)} \quad . \qquad (20)$$

After rearranging Eqn.(20) and taking into account the fact that, according to kinetic data[42] the order of the reaction with respect to the hydroperoxide is $n = 1$, we obtain

$$\frac{1}{w} = \frac{1}{k_{\text{decomp}} [M^{2+}]_0} + \frac{1}{k_{\text{decomp}} K [\text{ROOH}] [M^{2+}]_0} \quad . \qquad (21)$$

Eqn.(21) was used for the graphical evaluation of K and k_{decomp} (Table 3) from plots of 1/w against 1/[ROOH] (Lineweaver and Burk[47]) for the intermediate active complexes in the reactions of CHP with the Cu^{2+} or Co^{2+} complexes of monethanolamine, diethanolamine, triethanolamine, TEA, morpholine, etc.[42]

It has been shown that there are correlations between k_{decomp} and K_{form}—the formation constant of the complexes $(MA)^{2+}$ between A and M^{2+}, and also between the stability constant K_{st} and $\lg k_{\text{decomp}}$. The results demonstrate the validity of the selected model of the process for the test systems. Thus the M^{2+} complexes of amines and aminoalcohols $(MA)^{2+}$ in aqueous solutions behave as simple analogues of enzymes of the catalase type in the CHP and TBHP decomposition reactions. One must point out that these complex catalysts (particularly the complexes of monoethanolamine and pyridine) are also not consumed in the reactions and, behaving as models of enzymes, induce the continuous decomposition of ROOH.[42]

Table 3. The constants K and k_{decomp} for intermediate complexes of the type [E...ROOH] in the reactions of CHP with $(MA)^{2+}$.

	A	K, litre mol^{-1}	k_{decomp}, min^{-1}
TEA	(60°)	5.4	3.7
Morpholine	(80°)	3.5	58.8
Morpholine*	(80°)	6.0	6.7
Monoethanolamine	(78°)	3.7	18.2
Diethanolamine	(80°)	4.7	62.5
Triethanolamine	(60°)	2.5	66.7
Triethanolamine*	(80°)	2.2	4.0

*M = Co; in the remaining cases M = Cu.

3. The Effect of Monoethanolamine and Its Bivalent Copper and Cobalt Complexes on the Living Organism

It is known that the oxidation of organic substances (proteins, fats, carbohydrates, alcohols, etc.) in the living organism is regulated by various enzymes. The final stable products (H_2O, CO_2, N_2, etc.) of such oxidation are obtained mainly as a result of the decomposition of the intermediate nitrogen-containing and hydroperoxy-compounds. Enzymes containing in many instances the ions of "metals of life" (Cu^{2+}, Co^{2+}, Mn^{2+}, etc.) control the mechanism and rate of decomposition of these hydroperoxides by virtue of the specificity of their action[32].

Numerous investigations have shown[6,56] that, apart from certain biometals (for example, Cu^{2+} and Co^{2+}), monoethanolamine plays a definite biochemical role in the living organism. It has been established that the introduction of the above substances in microamounts separately or jointly into the living organism (both healthy and diseased) enhances its biochemical activity. For example, the growth and development of birds, calves, and plants are accelerated and a number of human diseases are cured (sugar diabetes, diseases of the liver, kidneys, heart etc.). The experimental data obtained indicate an appreciable intensification of the metabolism of substances, particularly when monoethanolamine is introduced together with Cu^{2+}. Monoethanolamine is also an active stimulant enhancing the egg laying capacity in chickens, etc.[8]

The use of monoethanolamine in the treatment of the chronic renal failure in man has a positive influence on functional parameters of the operation of kidneys such as diuresis, the secretion of urine, etc. Monoethanolamine is non-toxic in small doses and, on being introduced into the organism, sharply enhances its protective responses. Monethanolamine is capable of inhibiting the development of

cardiac hypertrophy without influencing the contracting function of the heart at the same time. It has been shown that the aminoalcohol does not stimulate the absorption of O_2 when glutamate is used as the respiratory substrate[8].

One should note that hitherto there has been no explanation in the literature of the wide variety of the positive effects of monoethanolamine (colamine) and its Cu^{2+} and Co^{2+} complexes on living organisms.

It follows from a number of studies[40–45,52–54] that, in aqueous solutions at temperatures starting from 30–40 °C, CHP and TBHP decompose at a moderate rate in the presence of amines and aminoalcohols. However, in the presence of monoethanolamine or M^{2+} alone[21,42,44] at temperatures up to 90 °C hydroperoxides hardly decompose, while in the joint presence of the above substances with $M^{2+} = Cu^{2+}$, Co^{2+}, Mn^{2+}, etc. CHP and TBHP are decomposed catalytically mainly via a non-radical mechanism. As already mentioned, the M^{2+} complexes of monoethanolamine of the type $(MA)^{2+}$ are "non-consumable" catalysts in the decomposition of ROOH under conditions where hydroperoxides are continuously added to the reaction system, i.e. the effect of the complexes $(MA)^{2+}$ can be identified with enzyme catalysis (naturally in a model form).

On the basis of the data obtained, we shall attempt to explain the role of monoethanolamine and its Cu^{2+} and Co^{2+} complexes in the living organism. The accumulation of hydroperoxides (or peroxides) in the living organism is an undesirable phenomenon, since their decomposition via a radical mechanism results in the formation of extremely active free radicals, which can decompose cells and can induce chemical changes in enzymes, proteins, etc.[57] Hydroperoxides thereby initiate definite biochemical modifying processes, which lead to functional damage in the organism.

To prevent such action of hydroperoxides, one must stimulate their decomposition, preferably in a continuous manner and via a non-radical mechanism[57]. This role is apparently played by monoethanolamine and its Cu^{2+} and Co^{2+} complexes, which catalyse the non-radical decomposition of hydroperoxides. "Biometals", in particular Cu^{2+} and Co^{2+}, are present in microamounts in the living organism and, when monoethanolamine is introduced (providing the amount of colamine in the organism is small), the above scattered ions are "collected" by monoethanolamine in the form of complexes.

Thus it is extremely likely that monoethanolamine, jointly with certain variable-valence metal cations (including Cu^{2+} and Co^{2+}), regulates the required level of hydroperoxides in the organism.

IV. THE MECHANISM OF THE REACTIONS OF HYDROPEROXIDES WITH AMINES AND AMINOALCOHOLS IN THE PRESENCE AND ABSENCE OF M^{2+}

In order to elucidate the mechanism of the reactions of ROOH and A and of ROOH, A, and M^{2+} in aqueous media, the final stable reaction products were identified, in addition to studies of the intermolecular interactions between the components of the reacting systems (determination of the compositions of the intermediate complexes) and the study of the kinetics.

Amines and aminoalcohols exhibit interesting properties in reactions with hydroperoxides (in the absence and presence of M^{n+}): (a) they react with hydroperoxides in both aqueous[40–42] and organic solvents with a high dielectric constant, for example, in amides[40–42,48,49]; (b) they are effective complex-forming agents (ligands) for metal cations, for example, Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, etc. The complexes $(MA)^{2+}$ induce the decomposition of hydroperoxides in an aqueous phase via a mechanism which sometimes resembles homogeneous enzyme catalysis[20,21,42,44]; (c) the products of the reactions of amines with hydroperoxides are in many instances of practical interest[40–42]; (d) certain aminoalcohols and their chelate complexes with bivalent copper, cobalt, etc. ions are stabilisers and hardening agents respectively for polychloroprene and butadiene-acrylonitrile (with an epoxy-resin) adhesives [50,51].

The nature of the products of reactions of ROOH, A, and M^{2+} depends on the nature of the amines and hydroperoxides, on the presence of M^{2+}, and also on the solvent[21,40–42,52]. In aqueous media the oxidation of amines by hydroperoxides (in the absence of M^{2+}) leads to the formation of an aminoaldehyde in 89.3% yield (in the case of CHP) [12] and the amine oxide (in the case of TBHP).[52] It has been shown by infrared spectroscopy and elemental analysis that the corresponding alcohols are then obtained from the hydroperoxides—phenylisopropyl alcohol (yield 97.6%) and t-butyl alcohol[21,23,54].

The simultaneous catalytic decomposition of the CHP dimer by the aminoalcohol (diethanolamine, triethanolamine, etc. except monoethanolamine) in aqueous media results in the formation of phenylisopropyl alcohol and oxygen in 9.6% yield[40,54].

As mentioned above, in the presence of variable-valence metal cations (Cu^{2+}, Co^{2+}, Mn^{2+}, etc.) the reactions between ROOH and amines are accompanied also by the catalytic decomposition of ROOH by the amine complexes $(MA)^{2+}$.[21,42,44] The latter reaction predominates—its rate is several times greater than the rates of the other two reactions. Identification of the final stable products of the reaction of ROOH, A, and M^{2+} in water by infrared spectroscopy, ^1H NMR, chromatography, polarography, volumetric measurements, and elemental analysis showed that the final products are phenylisopropyl alcohol (for CHP) or t-butyl alcohol (for TBHP) and oxygen (the yield of all the products was 99.6%).[54] In the presence of diethanolamine, triethanolamine, and other aminoalcohols involving the simultaneous occurrence of the above reactions (direct interaction between CHP and A and the decomposition of the cumenyl hydroperoxides dimer catalysed by the aminoalcohol molecule)[40], an aminoaldehyde is obtained apart from the corresponding alcohol and oxygen. The aminoaldehyde was determined polarographically by elemental analysis and by other methods[54]. In the presence of monoethanolamine and pyridine only one reaction catalysed by the metal–amine complex takes place and for this reason the aminoaldehyde was not detected among the products of the reactions of these amines. However, the polarograms obtained for the reaction between ROOH and an aminoalcohol in the absence and presence of M^{2+} show that the aldehyde is formed only via the first, direct reaction between ROOH and the aminoalcohol. These data agree with the earlier kinetic results[40–42].

On the basis of the data presented, we put forward mechanisms for the reactions investigated which are presented below [the charges of the species shown in the various schemes (RO_2^-, RO_3^-, etc.) reflect the tendency towards a redistribution of electron density].

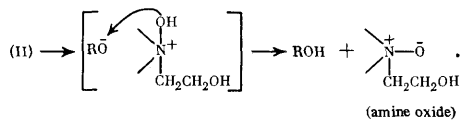
1. The First Reaction—Direct Interaction between ROOH and Aminoalcohols (except Monoethanolamine)

As an example, we shall consider the reaction of CHP with triethanolamine. As stated at the beginning of the review, the first step in the reactions of hydroperoxides with amines in water involves the formation of complex (II):

$$\mathrm{ROOH} + :\mathrm{N}- \rightleftarrows \text{(II)} \quad (22)$$

The mechanism of the decomposition of complex (II) to the products depends on the nature of R for given amine and solvent.

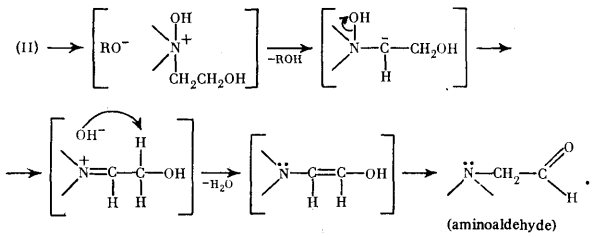
(a) R = $(CH_3)_3C$. The t-butyl group is electron repelling:



(23)

CH_3

(b) R = $C_6H_5-C-CH_3$. By virtue of the presence of the phenyl substituent, the phenylisopropyl group has distinct electron repelling properties and the mechanism can be represented in this instance in the following manner:



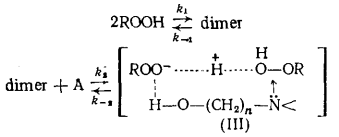
(23a)

2. Second Reaction—Decomposition of the Hydroperoxide Dimer Catalysed by the Aminoalcohol (except Monoethanolamine)

The rate of this reaction is described by an equation of type (4):[40]

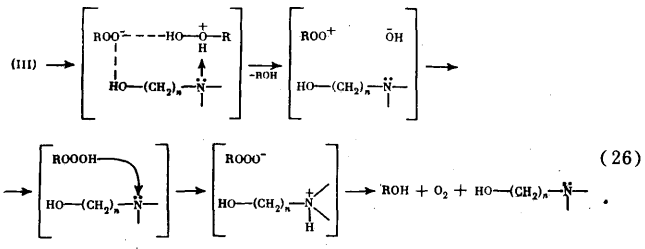
$$w_2 = k_{cat}[ROOH]^2, \qquad (24)$$

where $k_{cat} = k_2[A]$. The involvement of the cumenyl hydroperoxide dimer in the catalytic decomposition of CHP by the aminoalcohol has been established on the basis of this equation and kinetic data[12,40-42]:



(25)

It has been established[55] that alkali catalyses the decomposition of CHP in aqueous solution, the rate of decomposition being a maximum for $[ROOH]/[ROO^-] = 1$. In the intermediate complex (III) this ratio in fact obtains; the ROO^- group is an electron donor, while the O–O bond is an electron acceptor. Taking this into account, the following transformations within the complex, leading to the formation of the final stable products, have been postulated:



(26)

3. Third Reaction—Decomposition of Hydroperoxides Catalysed by the M^{2+}–Amine Complex

According to the present author[42], the cationic complex $(MA)^{2+}$ is catalytically active in the ROOH–A–M^{2+} reaction system. It is known[19] that amine complexes having the composition $[MA_n]^{2+}$, where $n = 4$ or 6, are thermodynamically active. In particular, when $M^{2+} = Cu^{2+}$, Co^{2+}, etc., $n = 4$ and the complex has the structure $[MA_4]^{2+}$.

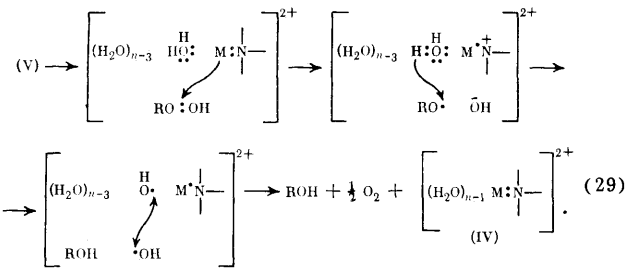
The following equilibria obtain in aqueous solutions[19]:

$$[MA_n]^{2+} \xrightleftharpoons{H_2O} [H_2OMA_{n-1}]^{2+} \xrightleftharpoons{H_2O} \cdots \xrightleftharpoons{H_2O} \underset{(IV)}{[(H_2O)_{n-1}MA]^{2+}}. \qquad (27)$$

However, the aquo-complex (IV) is catalytically active[21]. The reaction of complex (IV) with CHP and TBHP can be represented as follows:

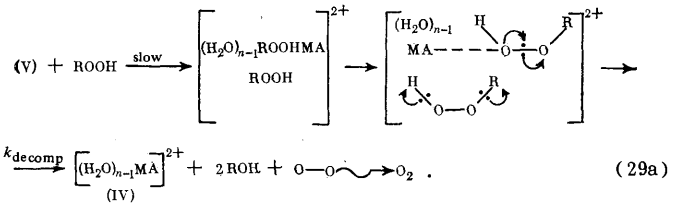
$$[(H_2O)_{n-1}MA]^{2+} + ROOH \xrightleftharpoons{fast} H_2O + \underset{(V)}{\left[(H_2O)_{n-3}H_2OMA\begin{matrix}\\ROOH\end{matrix}\right]^{2+}}. \qquad (28)$$

The transfer of one or two electrons from the aminoalcohol molecule to the hydroperoxide actually occurs in complex (V) via the catalyst cation:



(29)

The mechanism of the formation of the final products (the corresponding alcohols and oxygen) can be represented by another scheme[32] if it is assumed that the rate-limiting stage is the interaction of complex (V) with ROOH:



(29a)

Eqn.(9) shows that the order of the reaction with respect to M^{2+} is unity[44]. However, in many cases the order of the decomposition reaction of hydroperoxides catalysed by the complex $(MA)^{2+}$ is less than unity with respect to M^{2+}.[21] This can be explained by the equilibrium

$$(IV) + [MA]^{2+} \rightleftarrows \underset{(VI)}{[(H_2O)_{n-2}MA]^{2+}} + [(H_2OMA_{n-1}]^{2+}. \qquad (30)$$

According to a study by the present author[42], when $n \geq 2$, the complexes, including complex (VI), are inactive in the decomposition of hydroperoxides in an aqueous medium. Thus only complex (IV) is a catalytically active amine complex in the decomposition of ROOH in aqueous media.

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† $[(H_2O)MA]^{2+}$? (Ed.of Translation).

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The Splitting of the Silicon-Carbon Bond by Compounds of Platinum and Palladium

I.S.Akhrem, N.M.Chistovalova, and M.E.Vol'pin

Reactions involving the splitting of an Si-C bond under the influence of platinum and palladium complexes have been examined, and the mechanisms of these reactions discussed. It has been shown possible to use reactions involving the splitting of the Si-C bond in organic synthesis.
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I. INTRODUCTION

The extensive application of organosilicon compounds in various branches of industry has stimulated the search for new methods of synthesis. The considerable progress in this direction in the last 20–30 years has been related to the use of metal-complex catalysts, in particular compounds of platinum and its analogues, which are the most active catalysts for a wide range of reactions in the synthesis of organosilicon compounds. Among these reactions, a process of the greatest importance is hydrosilylation, which is a general method for the synthesis of organosilicon compounds of different classes. Heterogeneous systems containing platinum and palladium were first proposed as hydrosilylation catalysts in 1953.[1] The use of these catalysts made it possible to carry out the reaction between hydrosilanes and unsaturated compounds with functional groups; this had not been possible before, since the hydrosilylation methods used required high temperatures or the presence of radical initiators. Somewhat later, the use of hydrogen chloroplatinate as a highly effective hydrosilylation catalyst was proposed[2]. In 25 years, the range of catalysts has extended considerably, but even now, H_2PtCl_6 is most frequently used for the hydrosilylation of alkenes and alkynes. Alkene complexes of Pt^{II}, phosphine complexes of Pt^0 and Pd^0, complexes of platinum with silyl ligands and with polymeric ligands, and many others are also widely used[3]. Hydrosilylation can now be applied to practically all unsaturated compounds: simple alkenes and alkenes with functional groups, dienes, alkynes, and carbonyl compounds. Recently, this reaction has been used not only for the synthesis of organosilicon monomers and oligomers, but also for the conversion of linear and branched organosilicon polymers into polymers with a reticular structure. It is also acquiring importance for the synthesis of polycarbo-organosiloxanes[3]. In a number of cases, hydrosilylation is used industrially[4].

As well as the addition of hydrosilanes to unsaturated compounds, reactions involving the replacement of hydrogen on a silicon atom by other groups in the presence of platinum metal complexes are also of preparative importance. These reactions are used to obtain silanols, alkoxy- and aryloxysilanes, silyl ethers, siloxamines, silicon halides, etc.[5–11]

The reactions of hydrosilanes (and also metal-silyl derivatives of silicon) with platinum and palladium complexes form the basis of methods for synthesising complexes of these metals with silyl ligands[12–18]. The interest in platinum metal complexes containing group IVb elements is largely due to the promise of their practical application as catalysts.

Like silicon hydrides, compounds with a silicon–halogen bond can undergo oxidative addition to coordinatively unsaturated transition metal complexes, again giving silyl derivatives of the transition metals[17]. An interesting feature is that the splitting of a carbon–halogen bond under the influence of Pt^0 compounds can also take place in the coordination sphere of the metal, converting silyl complexes into silylene compounds[19].

In recent years, in addition to reactions accompanied by the splitting of Si–H bonds, reactions involving the splitting of Si–Si bonds have been used successfully in organosilicon synthesis. The disproportionation of disilanes to polysilanes in the presence of *trans*-$(Et_3P)_2PtCl_2$ was first detected in 1970.[20] A development of this work was the extensive use of the splitting of Si–Si bonds in disilanes, catalysed by triphenylphosphine complexes of platinum and palladium, "double silylation", to introduce two organosilicon groups into alkenes, 1,3-dienes, alkynes[21–25], and allenes[24].

The ability of Pd^0 complexes to catalyse the disproportionation of disilanes[26] has also been used to convert relatively easily accessible disilanes into monosilanes with functional groups by a reaction involving the combination of disilanes with halogen derivatives[27–29].

The transformations of organosilicon compounds under the influence of platinum and palladium complexes, examined above, include the splitting of both polar bonds Si–M and Si–Cl and non-polar bonds Si–H and Si–Si, and are used chiefly for the synthesis of organosilicon compounds. The last known review in this field is that of Curtis and Epstein[30].

In the last ten years, the activation and splitting of the even more inert Si–C bonds have been increasingly studied. Studies in this direction are opening up new possibilities for the use of organosilicon compounds in organic synthesis and as components of catalytic systems.

The urgency of this task is determined by the following features. Organic derivatives of silicon, unlike organometallic compounds, are stable to oxygen and moisture, do not ignite in air, and are generally non-toxic. On the other hand, organosilicon compounds are fairly readily accessible, and many of them are produced on the industrial scale. Thus the use of organosilicon compounds of the organometallic derivative type in organic synthesis or as components of catalytic systems is a promising field.

II. THE SPLITTING OF SILICON–CARBON BONDS IN ORGANOSILICON COMPOUNDS CONTAINING AN ACTIVATED Si–C BOND

1. The Removal of Unsaturated Groups from a Silicon Atom

The bonds formed by silicon with α,β-unsaturated compounds are more reactive than a silicon–alkyl bond. This is due to the increase in the polarity of the silicon–carbon bond when an alkyl group is replaced by an unsaturated group[31], and also to the instability of the products of the addition of electrophilic reagents to multiple bonds as a consequence of β-decomposition[32]. These bonds can be split by protonic and aprotic acids, halogens, and nucleophiles[32–35]. An important feature, however, is that vinyl-, allyl-, and alkynylsilanes readily undergo reactions which are not accompanied by the rupture of silicon–carbon bonds: hydrogenation, the addition of halogens and hydrogen halides, etc. The vinyl group is not removed from the silicon atom when unsaturated silanes are polymerised in the presence of peroxides, protonic and aprotic acids, and also Ziegler–Natta systems[31].

Studies of the transformations of unsaturated silanes, catalysed by Pt and Pd complexes, were begun more than ten years ago[36]. It has now been shown that a wide range of platinum and palladium complexes bring about the removal of unsaturated groups from the silicon atom. π-Complex formation is the first stage in these reactions, and in a number of cases the corresponding π-complexes of the unsaturated silanes have been isolated as stable products. Allyl-[37–38], vinyl-,[38,39] and ethynylsilanes[36,40] are split by platinum and palladium complexes at the bonds between silicon and the unsaturated groups. For example, allylsilanes react very rapidly with palladium chloride and acetate in proton-containing solvents, forming a π-allyl complex of palladium and organic splitting products[37]†:

$$Me_3SiCH_2CH{=}CH_2 + Li_2PdCl_4 \xrightarrow{MeOH,H_2O} \rightarrow (\pi\text{-}C_3H_5PdCl)_2 + Me_3SiOMe + (Me_3Si)_2O + C_3H_6 + HCl$$
$$32\%\ (81\%) \qquad 75\%\ (188\%) \qquad 25\%\ (63\%) \qquad 56\%\ (140\%)$$

The mechanism proposed by the authors includes the initial exchange of groups between the Si and Pd atoms with the formation of a chlorosilane and a σ-allyl and then a π-allyl complex of palladium:

$$R_3SiCH_2CH{=}CH_2 + PdCl_2 \rightarrow R_3SiCl + [CH_2{=}CHCH_2PdCl]$$
$$[CH_2{=}CHCH_2PdCl] \rightarrow (\pi\text{-}C_3H_5PdCl)_2 \rightarrow \text{products}$$
$$R_3SiCl + R'OH \rightarrow R_3SiOR' + HCl$$
$$R_3SiCH_2CH{=}CH_2 + HCl \rightarrow R_3SiCl + CH_3CH{=}CH_2 .$$

The overall reaction is not catalytic with respect to the palladium salt[37], but formally, the catalytic yield of splitting products, calculated relative to Li_2PdCl_4, is due to the splitting, taking place in parallel, of the allylsilanes under the influence of HCl, formed by the alcoholysis or hydrolysis of the chlorosilane.

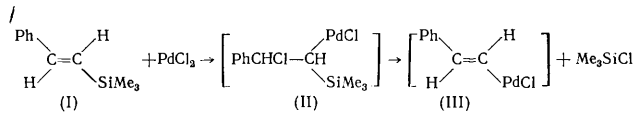
The benzonitrile complex of palladium $(PhCN)_2PdCl_2$ reacts with trimethylallylsilane, forming bis(η³-allyl)-μ-dichlorodipalladium and trimethylchlorosilane[38]:

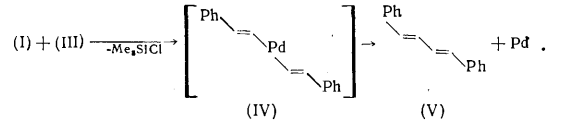
$$2\,Me_3SiCH_2CH{=}CH_2 + 2(PhCN)_2PdCl_2 \xrightarrow[-4\,PhCN]{} \left(HC(CH_2)(CH_2)\text{—}Pd\text{—}Cl\right)_2 + 2\,Me_3SiCl .$$

The reaction is quantitative in 3 d at 20°.

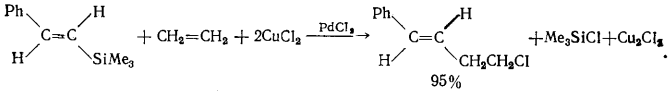
† The yields are given relative to the original silane, and in brackets relative to Li_2PdCl_4.

Interesting transformations take place with vinylsilanes under the influence of palladium chloride. In the presence of palladium chloride at room temperature, oxidative combination of β-trimethylsilylstyrene (I) takes place with the formation of *trans*, *trans*-1,4-diphenyl-1,3-butadiene (V).[39] In the presence of copper(II) chloride, the reaction is catalytic. The authors postulate the intermediate formation of organic derivatives of palladium (II)–(IV):

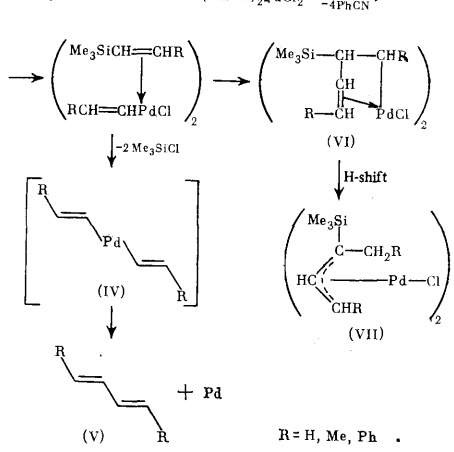




In the presence of an alkene and an excess of copper(II) chloride, chloroethylation products are formed, by analogy with Heck's chloroethylation reactions[41]:



The reaction of vinylsilanes with the benzonitrile complex of palladium in benzene shows an interesting feature: in addition to the products of oxidative combination, it gives a new π-allyl complex of palladium (VII) in 26% yield[38]:



According to the scheme proposed by the authors, the reaction giving divinylpalladium (IV) competes with the insertion of the alkene at the Pd–C bond, which gives an unstable compound (VI). The final π-allyl complex of palladium (VII) is formed as a result of the stabilisation of compound (VI) by a hydrogen shift.

Zeise's salt $K[PtCl_3(C_2H_4)]$ catalyses the removal of vinyl and allyl groups from a silicon atom in boiling absolute ethanol[36]. For the reaction of trimethylvinylsilane with Zeise's salt[42] it was proved that π-bonding is the first stage in the splitting of unsaturated silanes. In acetone, a π-complex containing trimethylvinylsilane has been isolated quantitatively and characterised:

$$Me_3SiCH{=}CH_2 + K[PtCl_3(C_2H_4)] \rightarrow K[PtCl_3(Me_3SiCH{=}CH_2)] + C_2H_4 .$$

In moist acetone this compound undergoes splitting of the Si-vinyl bond to give Zeise's salt and hexamethyldisiloxane:

$$K[PtCl_3(Me_3SiCH{=}CH_2)] + \frac{1}{2}H_2O \rightarrow K[PtCl_3(C_2H_4)] + \frac{1}{2}(Me_3Si)_2O .$$

The formation of π-complexes of vinyl- and ethynylsilanes have also been observed when unsaturated silanes are treated with other Pt^0 and Pt^{II} compounds such as $Pt(C_2H_4)_2(PR_3)$,[43] $(Ph_3P)_2Pt(C_2H_4)$,[40,44] and $PtCl_2(C_2H_4)Py$.[45] A comparison of vinylsilane complexes of Pt^0 and Pt^{II} [44] showed that the Pt^0 complexes are more stable to splitting.

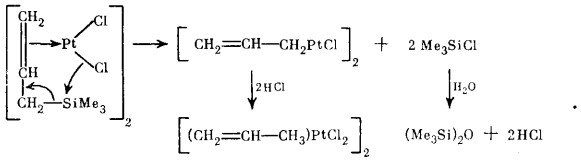
In 1976, French chemists[45] made a detailed study of the reactions of unsaturated silanes with the general formula $Me_3Si(CH_2)_nCH=CH_2$ ($n = 0, 1, 2$) with the dimeric platinum complex $Pt_2Cl_4(C_2H_4)_2$. As in most of the reactions described above, the first stage in this case is ligand exchange to give a new Pt^{II} complex containing an unsaturated silane as ligand. The activated silicon–carbon bond is then split. Thus in the reaction of $Me_3SiCH_2CH=CH_2$ with $Pt_2Cl_4(C_2H_4)_2$ in the presence of water at 20° (molar ratio silane : platinum complex : water = 2 : 1 : 1), the silane is converted quantitatively into hexamethyldisiloxane and propene:

$$2Me_3SiCH_2CH{=}CH_2 + H_2O \xrightarrow{[Pt]} 2CH_3CH{=}CH_2 + Me_3SiOSiMe_3 .$$

The reaction of allylsilane with $Pt_2Cl_4(C_2H_4)_2$ takes place catalytically at 20° in 10 d (molar ratio silane : complex : water = 20 : 1 : 10). For all the silanes studied, in the stoichiometric reaction with the dimeric platinum complex, a rapid equilibrium is first established, with the formation of the π-complex. At $n = 2$, the crystalline complex of the silane with $PtCl_2$ was isolated:

$$2\,Me_3Si(CH_2)_nCH{=}CH_2 + Pt_2Cl_4(C_2H_4)_2 \rightleftarrows \left[\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ (CH_2)_nSiMe_3 \end{array}\!\!\rightarrow PtCl_2\right]_2 + 2C_2H_4 .$$

The splitting of the vinyl- and allylsilanes by the dimeric platinum complex is attributed[45] to the decomposition of an intermediate π-complex in which the platinum atom creates a positive charge in the β-position relative to silicon.

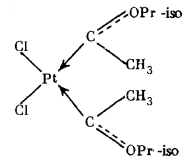


This explains the observed stability of the complex with butenylsilane $Me_3Si(CH_2)_2CH=CH_2$, in which a positive centre is created in the γ- and δ-positions relative to the silicon atom. In the proposed scheme, Pt^{II} acts as a π-acid. An interesting feature is that in the splitting of silanes, Pt^{II} has been found to be a stronger acid than protonic acids such as CF_3COOH and HCl. The phosphine complex $Pt_2Cl_4(Ph_3P)_2$ is also active in reactions with $Me_3Si(CH_2)_nCH=CH_2$. Its reaction with allylsilane in aqueous $CDCl_3$ at 20° leads to slow splitting of the silane to give hexamethyldisiloxane (90% after 60 h).[45] Pt^{II} complexes can also split Si–C_{sp} bonds[36]. Thus the reaction of $Pt_2Cl_4(C_2H_4)_2$ with $PhC{\equiv}CSiMe_3$ in dry benzene at 20° in an atmosphere of nitrogen gives a deeply coloured complex containing platinum; its infrared spectrum shows a band corresponding to the frequency of the ethyne group $\nu = 2070$–$2110\ cm^{-1}$:

$$2PhC{\equiv}CSiMe_3 + Pt_2Cl_4(C_2H_4)_2 \xrightarrow{60°} 2Me_3SiCl + 2C_2H_4 + 2PhC{\equiv}CPtCl .$$

In boiling alcohol, the ethynyl group is removed from the silicon atom under the influence of catalytic quantities of the complexes $Pt_2Cl_4(C_2H_4)_2$ or $K[PtCl_3(C_2H_4)]$. Under these conditions, allylsilanes are split even more easily[36].

The reactions of ethynylsilanes with platinum complexes are sometimes unusual, and do not reduce to a simple scheme including π-complex formation with the subsequent elimination of unsaturated compounds. An example[46,47] is the interesting transformation of trimethylethynylsilane under the influence of H_2PtCl_6 in isopropyl alcohol at 20° into an alkoxycarbene complex of Pt^{II}, whose structure was established by X-ray diffraction:

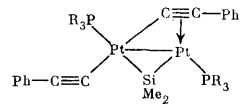


The reaction is accompanied by rupture of the Si–C bond. The resulting complex is a good catalyst for the hydrosilylation of alkynyl compounds.

The reaction of $Me_2Si(C{\equiv}CPh)_2$ with the platinum(0) complex $[Pt(C_2H_4)_2(PR_3)]$ is also extremely unusual[40]. In this case, both phenylethynyl groups are removed from the silicon atom to give a diplatinum complex containing all the fragments of the organosilicon molecule:

$$Me_2Si(C{\equiv}CPh)_2 + 2Pt(C_2H_4)_2(PR_3) \rightarrow [Pt_2(Me_2Si)(C{\equiv}CPh)_2(PR_3)_2] + 4C_2H_4 .$$
$$R = C_6H_{11}$$

X-Ray diffraction showed that the platinum atoms in this complex are not equivalent; one of them (formally Pt^{IV}) is joined by σ-bonds to the dimethylsilyl and two phenylethynyl groups, and the other platinum atom (formally Pt^{II}) is joined by a σ-bond to the dimethylsilyl groups and by a π-bond to one of the phenylethynyl groups:



This reaction is of interest as the first rigorously proved example of the oxidative addition of an Si–C bond to a transition metal atom.

2. The Rupture of Silicon–Carbon Bonds in Strained Cyclic Silanes and Disilanes

Platinum and its derivatives Pt/C, H_2PtCl_6, and $(C_2H_4)_2$. Pt_2Cl_4 catalyse the splitting on of an Si–C bond in strained organosilicon heterocyclic compounds such as sila- and 1,3-disilacyclobutanes to give telomerisation and polymerisation products[48–50]. Thus silacyclobutanes are converted into polymers by heating with catalytic quantities of Pt/C or H_2PtCl_6 at 50–100° [49]:

$$nR^1R^2Si\begin{array}{l}CH_2\\CH_2\end{array}CHR^3 \xrightarrow{[Pt]} -(-R^1R^2SiCH_2CHR^3CH_2-)_n- .$$

The dimeric ethlene complex $(C_2H_4PtCl_2)_2$ is effective in this reaction even at room temperature[50]. Disilacyclobutanes in the presence of platinum catalysts are polymerised at 100 to 150°:

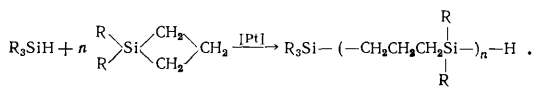
$$nMe_2Si\begin{array}{l}CH_2\\CH_2\end{array}SiMe_2 \xrightarrow[150°]{[Pt]} -(-Me_2SiCH_2-)_n- .$$

In the absence of catalysts, polymerisation does not take place at this temperature.

With 1,1-dimethyl-1-silacyclopentane, polymerisation on platinum does not take place up to 200°, and the silacyclohexanes $CH_2-(CH_2)_4-SiH_2$ and $CH_2(CH_2)_4-SiMeH$ are not split under the influence of platinum and palladium catalysts at

500°.[51] Thus the driving force of the splitting of Si–C bonds in sila- and disilacyclobutanes is the strain in the four-membered ring.

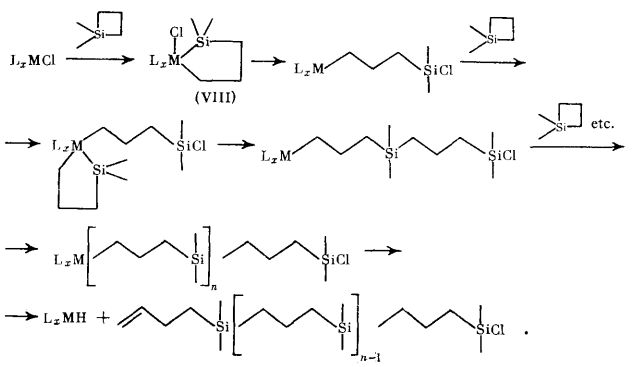
In the presence of platinum catalysts, silacyclobutanes and disilacyclobutanes react with hydrosilanes at 50–100° to give telomers:



$n = 1, 2$

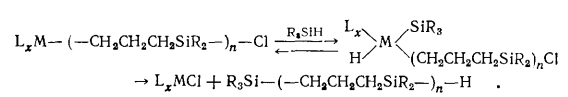
This reaction can be regarded as an example of alkyl-hydrogen ligand exchange at a silicon atom under comparatively mild conditions. Without the catalyst, it takes place at a higher temperature.

The role of the transition metal in the homogeneous catalytic polymerisation of strained organosilicon heterocyclic compounds has been studied[50]. A mechanism including the following successive stages was proposed: the oxidative addition of the silacyclobutane to the transition metal complex to give a metal-containing ring (VIII); splitting of the M–Si bond, accompanied by the migration of halogen from M to Si and opening of the ring; growth of the polymer chain as a result of the insertion of a new molecule of silacyclobutane at the M–C bond; and chain termination by the ejection of a hydrogen atom from the β-position relative to the metal:

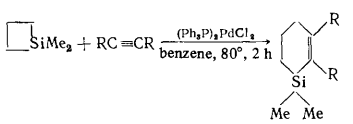


(VIII)

The formation of telomeric products can be explained similarly.



Interesting reactions involving the cyclo-addition of silacyclobutanes to alkynes in the presence of palladium catalysts have also been described[52].



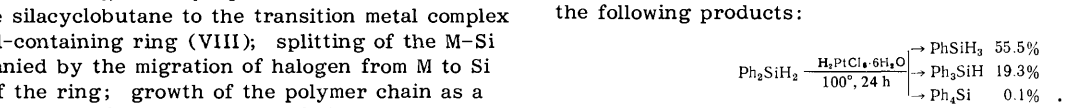
R=COOMe .

Pd^{II} and Pd^{0} complexes are effective in these reactions: $PdCl_2(PhCN)_2$, L_4Pd, L_2Pd(alkene), and metallic Pd. The authors suggest that the driving force of these reactions is again the strain in the silacyclobutane ring, since silacyclopentanes and other non-strained silacyclanes do not react with alkynes.

3. Rupture of Silicon–Carbon Bonds in Hydrosilanes

Hydrosilanes can disproportionate when heated or under the influence of Lewis acids. The ease of the disproportionation of hydrosilanes compared with tetra-alkyl(aryl)-silanes is due to the ease of formation of five- and six-co-ordinate complexes of silicon in the case of the hydrosilanes, since for these the geometric and electronic factors are more favourable than for tetraorganosilanes. In five- and six-co-ordinate complexes of silicon, the rupture of Si–H and Si–C bonds is facilitated. The tendency for these complexes to be formed increases with increase in the number of hydride hydrogen atoms in the molecule and with increase in the acceptor power of the groups joined to silicon.

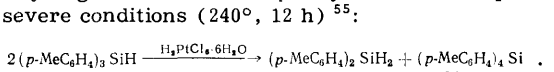
The disproportionation of diphenylsilane in the absence of catalysts is observed at 160°. Lewis acids ($AlCl_3$, $ZnCl_2$) catalyse these transformations under milder conditions[53]. Platinum derivatives also catalyse the disproportionation of hydrosilanes[53]. Thus in the presence of catalytic quantities of H_2PtCl_6 at 100°, diphenylsilane disproportionates to give the following products:



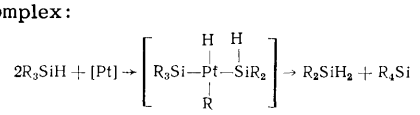
PtO_2 and metallic platinum are also effective in this reaction.

$PhSiH_2Cl$ begins to disproportionate under the influence of H_2PtCl_6 even at room temperature, $PhSiHCl_2$ at 50°, and Ph_2.SiHCl at 200°.[54] K_2PtCl_4 and K_2PtCl_6 also show catalytic activity in these reactions.

The disproportionation of tri-*p*-tolylsilane in the presence of H_2PtCl_6 to give di- and tetra-*p*-tolylsilanes takes place under severe conditions (240°, 12 h)[55]:

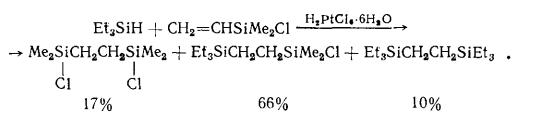


Disproportionation is not observed under these conditions in the absence of H_2PtCl_6. In the authors' opinion, the reaction mechanism includes the rupture of the Si–H and Si–tolyl bonds with retention of these fragments in the sphere of the platinum complex:

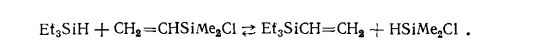


The authors cited[54,55] consider that the hydrosilane not only reduces Pt^{IV} to Pt^{II} but also takes part in the formation of the active complex. The formation of the various products is thermodynamically determined.

Several reactions have been described, in which the hydrosilylation of unsaturated compounds, in addition to the main processes, involves parallel processes with splitting of an Si–C bond. Thus the reaction of Et_3SiH with $CH_2=CHSiMe_2$.Cl in the presence of H_2PtCl_6 [55] gives a mixture of products:



The formation of side products can be explained if it is assumed that vinyl-hydrogen exchange takes place at the silicon atom:



In the reaction of $(Me_3SiO)_2SiMeH$ with hex-2-ene in the presence of $H_2PtCl_6.6H_2O$ at 140°, in addition to the "normal" hydrosilylation product $(Me_3SiO)_2SiMeC_6H_{13}$, the side products $(Me_3SiO)_3SiH$, $Me_3SiOSiMe_2C_6H_{13}$, and $Me_3SiOSiMe_2H$ were detected[56]. To explain the formation of the latter, it must be assumed that intermolecular exchange of Me_3SiO and Me groups takes place at the silicon atom:

$$2(Me_3SiO)_2SiMeH \xrightarrow[140°]{[Pt]} Me_3SiOSiMe_2H + (Me_3SiO)_3SiH$$
$$\downarrow \text{hex-2-ene}$$
$$Me_3SiOSiMe_2C_6H_{13}$$

In the extensive literature devoted to hydrosilylation reactions, however, very little mention is made of the anomalous products obtained by the splitting of Si–C bonds.

III. THE SPLITTING OF SILICON–ALKYL AND SILICON–ARYL BONDS BY Pt AND Pd COMPOUNDS

A silicon–carbon bond not containing activating groups is fairly inert in homolytic and heterolytic reactions. The reactivity of the silicon–alkyl bond resembles most closely that of the carbon–carbon bond in alkanes. In homolytic reactions in tetra-alkylsilanes, as a rule, the carbon–hydrogen bond, and not the silicon–alkyl bond, is broken preferentially[33,51,57]. Tetra-alkylsilanes also have a high thermal stability. Tetramethylsilane decomposes at 700°, and methyldibutylsilane only at 1000°.[57] Substituted alkylsilanes, in particular β-halogenoalkylsilanes, are much less stable to heat[51].

The silicon–carbon bond is more sensitive to electrophilic and nucleophilic reagents than the carbon–carbon bond. This is due to the slight polarity of the Si–C bond and the ability of the silicon atom to increase its co-ordination number, facilitating attack by a base at this atom. Nevertheless, in these reactions also, the silicon–alkyl bond is chemically fairly inert. Thus under ordinary conditions, tetra-alkylsilanes are not affected by alkali metals, organometallic compounds, metal hydrides, and alkalis and acids of medium strength[35,51].

The chemical inertness of the Si–Alk and Si–Ar bonds is greater than that of the vinyl, allyl, ethynyl, and other activated Si–C bonds examined in section II. The problem of the metal-complex activation of Si–Alk and Si–Ar bonds therefore appears most difficult.

1. Transformations of Silanes Under the Influence of Pt^{IV} and Pd^{II} Complexes

The splitting of an Si–Alk bond was first detected[58] by the action of Pt and Pd derivatives on hexamethyldisiloxane. When hexamethyldisiloxane is heated in the presence of 0.01 to 1% of a catalyst, octamethyltrisiloxane is formed:

$$Me_3SiOSiMe_3 \xrightarrow{\text{catalyst}} Me_3SiOSiMe_2OSiMe_3 .$$

Methane is detected in the gas phase.

Under the same conditions in the absence of a catalyst, octamethyltrisiloxane and methane are not formed from the disiloxane. The reaction takes place both in solvents (alcohol, benzene) and without a solvent, and takes place to a slight extent even at 100°. The yield of octamethyltrisiloxane after 10 h at 200° is 10–20%, calculated relative to the original hexamethyldisiloxane. Catalytic activity in this reaction is shown by a fairly wide range of platinum and palladium compounds: $H_2PtCl_6.6H_2O$, $(Ph_3P)_4Pt$, $(Ph_3P)_3Pt$, $PdCl_2$, Pt/C, etc.

Subsequently, the possibility of splitting the Si–C bond under the influence of platinum and palladium complexes in organosilicon compounds not containing functional groups—tetra-alkyl- and trimethylarylsilanes—was studied[59–67]. The transformations of the following silanes were examined: Me_4Si, Me_3SiEt, Me_3SiPr, Me_3SiBu, $Me_3SiC_6H_4X$ (X = H, *p*-Me, *p*-MeO, *p*-Cl, *m*-Me, *m*-MeO, *m*-Cl). Chloro-complexes of platinum and palladium in different oxidation states $PtCl_4$, $H_2PtCl_6.6H_2O$, Na_2PtCl_6, $PtCl_2$, K_2PtCl_4, $(Ph_3P)_2PtCl_2$, $(Py)_2PtCl_2$, $(Ph_3P)_2Pt_2Cl_4$, *trans*-$[Pt(CO)Cl(Ph_3P)_2][ClO_4]$, $Pt_2Cl_4(C_2H_4)_2$, $PdCl_2$, $LiPdCl_3$, Li_2PdCl_4, and $(PhCN)_2PdCl_2$, metallic Pt and Pd, and triphenylphosphine complexes of Pt^0 and Pd^0, $(Ph_3P)_4Pt$ and $(Ph_3P)_4Pd$, were studied. It was found[59–63] that the silicon–carbon bond can be split unexpectedly easily by platinum(IV) and palladium(II) chlorides: $PtCl_4$, H_2PtCl_6, $PdCl_2$, $LiPdCl_3$, Li_2PdCl_4, and $(PhCN)_2PdCl_2$. Compounds of these metals in lower oxidation states ($PtCl_2$, K_2PtCl_4, $(Ph_3P)_2PtCl_2$, $(Ph_3P)_4Pt$, $(Ph_3P)_4Pd$, Pt/C, Pt black) have a low activity or are completely inactive.

Under the influence of $PtCl_4$ or $PdCl_2$ in organic solvents containing a small quantity of water, tetraorganosilanes are split to give the hydrocarbon and the hexa-alkyldisiloxane as main products:

$$2Me_3SiR + H_2O \xrightarrow[60–120°]{MX_n} 2RH + Me_3SiOSiMe_3$$
$$MX_n = PtCl_4, H_2PtCl_6, PdCl_2, LiPdCl_3, Li_2PdCl_4, (PhCN)_2PdCl_2 .$$

Organic chlorides and products of radical decomposition are formed in parallel to a slight extent in a number of cases.

The disiloxane formed is also demethylated under the influence of these complexes. For example, in the reaction of Me_4Si with $PtCl_4.3H_2O$ in benzene at 80°, octamethyltrisiloxane is formed in addition to methane and hexamethyldisiloxane.

Special experiments showed that HCl does not catalyse these reactions, that is in this case metal-complex activation, and not acid activation, of the Si–C bonds take place. The reactions take place under mild conditions, and the degree of conversion reaches 90%.

The role of the solvent is different in the reactions of silanes with Pd^{II} and Pt^{IV} chlorides. With the palladium complexes, silanes react readily in the most varied solvents (alcohols, THF, DMF, MeCN, benzene). In the reactions of silanes with $PtCl_4$, on the other hand, the nature of the solvent is more significant. Thus in the reaction of Me_3SiBu with $PtCl_4.3H_2O$, the degree of conversion of the silane is 80% in $CHCl_3$, 50% in benzene, and 14% in DMF, and the reaction does not take place in EtOH and Et_2O.[62] The passivating influence of donor solvents was attributed to their ability to form stable coordinatively saturated solvates with the metal salt.

An interesting feature is that the splitting of silanes is highly selective: in trimethylarylsilanes the aryl group is removed exclusively, and in mixed trimethylalkylsilanes practically only the methyl group is removed. The authors discuss the possible mechanism of this reaction, and suggest that the splitting of the Si–C bond by platinum and palladium chlorides takes place as an exchange reaction, giving the trialkylchlorosilane and an unstable organic derivative of the transition metal[62]:

$$Me_3SiR + MCl_n \rightarrow Me_3SiCl + [RMCl_{n-1}]$$
$$Me_3SiCl + \frac{1}{2}H_2O \rightarrow \frac{1}{2}Me_3SiOSiMe_3 + HCl .$$

The intermediate organic derivative of the transition metal can decompose further by two routes: it can undergo protolysis with the formation of the hydrocarbon and the regeneration of the metal chloride, or it can give organic chlorides

and the products of radical decomposition#:

$$[RMCl_{n-1}] + HCl \rightarrow RH + MCl_n$$
$$[RMCl_{n-1}] \rightarrow \begin{cases} \rightarrow RCl + MCl_{n-2} \\ \rightarrow R^{\cdot} + MCl_{n-1} \end{cases}$$

The reactions of Me_4Si with $PtCl_4$ in benzene or of Me_3SiPh with Li_2PdCl_4 in DMF in the presence of alcohols labelled with deuterium (ROD) give the hydrocarbons MeD and PhD respectively, containing a high percentage of deuterium (up to 80% of the theoretical yield). Thus in the presence of a source of protons, the principal direction of the decomposition of the intermediate organometallic compound is its protolysis, leading to the regeneration of the original transition metal complex. This route opens up the possibility of carrying out a catalytic reaction. In fact, in the presence of small quantities of added alcohol or water, the reactions of silanes with Pt and Pd chlorides take place catalytically[62]. A high activity is shown by H_2PtCl_6 in acetonitrile (Table 1) and by palladium(II) chloride in DMF (Table 2).

Table 1. Catalytic reactions of tetraorganosilanes with platinum compounds[62].

Silane	Catalyst	t, °C	τ, h	α	Solvent	A
Me_4Si	$H_2PtCl_6 \cdot 6H_2O$	150	10	100	MeCN *	14
Me_3SiEt	$PtCl_4 \cdot 3H_2O$	80	20	20	$PhNO_2$ *	12
Me_3SiPr	$PtCl_4 \cdot 3H_2O$	80	20	20	C_6H_6	4,4
Me_3SiBu	$PtCl_4 \cdot 3H_2O$	80	20	20	C_6H_6	6
Me_3SiBu	$PtCl_4 \cdot 3H_2O$	80	20	20	C_6H_6	17
Me_3SiBu	$H_2PtCl_6 \cdot 6H_2O$	120	20	1000	MeCN	20
Me_3SiPh	$H_2PtCl_6 \cdot 6H_2O$	150	20	1000	MeCN	130
Me_3SiPh	Pt/C	100	50	30	EtOH	32

Symbols. Here and in later Tables: τ is the reaction time, α the molar ratio Me_3SiR : catalyst, and A the degree of conversion of the silane, moles per mole of catalyst.

* [EtOH] = 0.5 M.

Although the presence of small quantities of water or alcohol is a necessary condition for catalysis, large quantities of these reagents inhibit the reactions.

The reactions of silanes with Pd^{II} can be converted into catalytic reactions by another method, by oxidising the precipitated metal by external oxidising agents ($CuCl_2$, p-benzoquinone), but the stability of the system is low: the degree of conversion of the silane does not exceed 7 moles per mole of Li_2PdCl_4 (see Table 2).

The behaviour of platinum and palladium compounds towards the silicon–carbon bond differs significantly from that of other transition metals, in particular the metals of the 3*d* series in their principal oxidation states[58–63]. The latter activate chiefly the splitting of arylsilanes, whereas Pt and Pd compounds split both Si–Ar and Si–Alk bonds[61].

For the reactions of silanes with $PtCl_4$, it is apparently necessary to take account of the possibility of the equilibrium $RPtCl_3 + PtCl_2 \rightleftharpoons RPtCl + PtCl_4$, although at a high temperature it is displaced to the left[68].

The kinetics and mechanism of the splitting of the silicon–aryl bond in Me_3SiAr, catalysed by Li_2PdCl_4 in DMF in the presence of 0.7% H_2O, have been studied[63]. At 80–100°, the reactions take place exclusively with the splitting of the Si–Ar bond to give hexamethyldisiloxane and the corresponding aromatic hydrocarbon:

$$2Me_3SiC_6H_4X + H_2O \xrightarrow{Li_2PdCl_4} Me_3SiOSiMe_3 + 2C_6H_5X$$
X = H, *p*-Me, *p*-Cl, *p*-MeO, *m*-Me, *m*-Cl, *m*-MeO .

The rates of the reactions of trimethylarylsilanes (except Ar = *p*-$MeOC_6H_4$) with Li_2PdCl_4 are described by an equation of first order with respect to the silane; the order of the reaction with respect to Li_2PdCl_4 in all cases was 0.5:

$$w = k\,[Me_3SiAr]\,[Li_2PdCl_4]^{0.5} .$$

The catalyst for the reaction is not the original complex, but the complex of $LiPdCl_3$ with DMF, formed by solvolysis[69]:

$$PdCl_4^{2-} + L \rightleftarrows PdCl_3(L)^- + Cl^-$$
L = DMF .

A characteristic feature of this reaction is that its rate is not sensitive to the nature of the substituent in the aromatic ring.

Table 2. Catalytic reactions of silanes with Pd^{II} compounds at 100°.[62]

Silane	Catalytic system	τ, h	α	Solvent	A
Me_4Si	Li_2PdCl_4	50	200:1	DMF*	150
Me_3SiPh	Li_2PdCl_4	50	1000:1	DMF	200
Me_3SiBu	Li_2PdCl_4	10	10:1	EtOH	2
Me_3SiBu	Pd(II)—$FeCl_3$—LiCl	10	10:1:10:10	EtOH	2
Me_3SiBu	Pd(II)—$C_6H_4O_2$—LiCl	10	10:1:10:10	EtOH	3.5
Me_3SiBu	Pd(II)—$CuCl_2$—LiCl	40	10:1:10:10	THF	1.3
Me_3SiBu	Pd(II)—$CuCl_2$—LiCl	10	10:1:10:10	EtOH	4.4
Me_3SiBu	Pd(II)—$CuCl_2$—LiCl	20	10:1:10:10	EtOH	7

* $[H_2O] = 0.4$ M.

Table 3. Influence of substituents in the splitting of Si–Ar bonds in $Me_3SiC_6H_4X$ under the influence of Li_2PdCl_4 in DMF at 100° (k'_{rel}) and under the influence of acids (k''_{rel}).

X	k'_{rel} (Ref.69)	k''_{rel} (Ref.70)
m-MeO	0.7	0.01
p-Cl	1.4	0.1
m-Cl	0.7	0.4
H	1	1
m-Me	0.8	2.3 (36.6) *
p-Me	2.6	23 (116,3) *
p-MeO	(1.2) **	1510

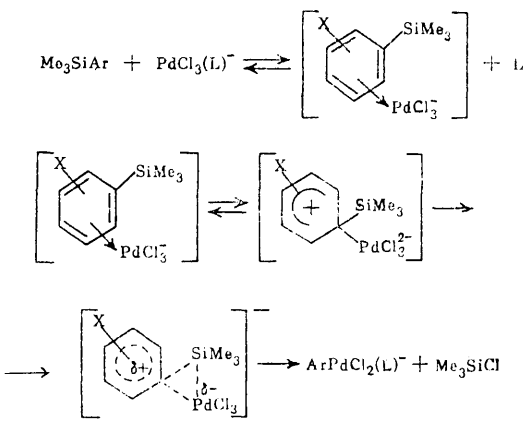
* Figures in brackets for the reaction with $FeCl_3$ in MeCN.[71]

** Ratios of the average reaction rates after 2 h taken.

Table 3 gives the relative rates of the splitting of trimethylarylsilanes under the influence of Li_2PdCl_4 in DMF and under the influence of electrophilic reagents. It can be seen from Table 3 that the position and nature of the substituents

have very little influence on the rate of splitting of the silanes under the influence of Li_2PdCl_4: silanes of the *meta*-series react at practically identical rates, irrespective of the nature of the substituent (*m*-Me, *m*-Cl, *m*-MeO). Substituents in the *para*-position, both electron donors (*p*-Me) and electron acceptors (*p*-Cl), increase the reaction rate slightly relative to non-substituted phenylsilanes. On the other hand, the rate of the acid splitting of the Si–Ar bond is extremely sensitive to the nature of the substituent, and the values of ρ in this case reach −5. An even greater influence of the substituents is observed in the reaction of trimethylarylsilanes with $FeCl_3$.

The following scheme was proposed for the splitting of Si–Ar bonds under the influence of Li_2PdCl_4 in aqueous DMF [69]:



$$2\,Me_3SiCl + H_2O \longrightarrow Me_3SiOSiMe_3 + 2\,HCl$$

$$ArPdCl_2(L)^- + HCl \longrightarrow ArH + PdCl_3(L)^-$$

L = DMF .

According to this scheme, the reaction involves the formation of a cyclic intermediate state with a low polarity. This suggestion agrees with the levelling of the influence of substituents, the low value of the enthalpy of activation (20.1 kcal mole^{-1}), the fairly high negative orientational entropy of activation (−27.2 e.u.), and the fact that the reaction rate is independent of the ionic strength of the solution, observed for the reaction of Me_3SiPh with Li_2PdCl_4 in DMF at 80–100°.

The authors suggest that the specific character of the action of the Pd^{II} complex on the Si–Ar bond is due to its biphilic character, that is its ability not only to accept electrons from the carbon atom but also to take part in a co-ordinative interaction with the silicon atom, as a result of which palladium simultaneously activates both atoms of the Si–C bond. Special calculations for geometric models of the corresponding σ-complexes showed that the Pd–Si distance in them is 3.20 Å, which is much less than the sum of the van der Waals radii of Pd and Si, equal to 4.25 Å. Thus the calculation of the model is consistent with the suggestion that there is a co-ordinative Pd–Si interaction[69].

The subsequent stages of the reaction involve the formation of an aryl palladium complex, which undergoes protolytic decomposition to give the final products and regenerate the catalyst. The intermediate formation of the σ-organic derivative of palladium is confirmed by the methylation and phenylation of alkenes by organosilicon compounds[59,60]. Thus in the presence of $PdCl_2$, the hydrogen at the double bond in styrene and cyclohexene is replaced by the methyl or phenyl group of an organosilicon compound:

$$R_3SiR' + PdCl_2 \rightarrow R_3SiCl + [R'PdCl]$$

$$[R'PdCl] + \underset{H}{\overset{}{\rangle}}C{=}C\langle \rightarrow \underset{R'}{\overset{}{\rangle}}C{=}C\langle + HCl + Pd$$

R′=Me, Ph .

The reactions take place very slowly even at room temperature, and at 100° and above, the yields of the products may be fairly high. Thus styrene can be methylated by tetraorganosilanes (Me_4Si, Me_3SiEt), silazane, and siloxanes. The methylating power of organosilicon compounds changes in approximately the same sense as the ease of splitting of the Si–C bond by electrophilic reagents:

$$Me_4Si\,(66\%),\ Me_3SiEt\,(66\%) > Me_3SiNHSiMe_3\,(52\%) > > Me_3SiOSiMe_3\,(34\%) > Me_3SiCH_2Cl\,(32\%) > > (Me_2SiO)_3\,(3\%) > Me_3SiCl\,(0\%)\ .$$

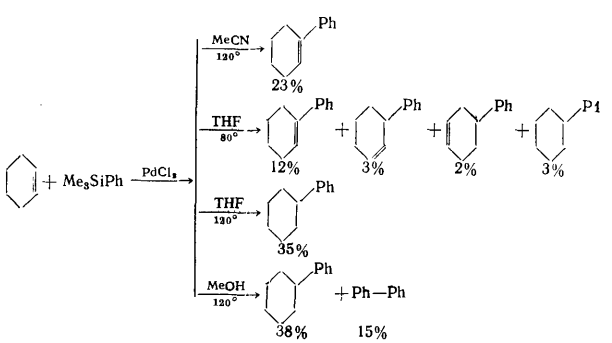
The chief product is that formed by the replacement of the β-hydrogen of styrene. The phenyl group in Me_3SiPh is removed more readily than the methyl group. It is also more readily transferred to the alkene. Examples of the phenylation of alkenes under the influence of Me_3SiPh are given in Table 4.

Table 4. Phenylation of alkenes under the influence of Me_3SiPh*. [60]

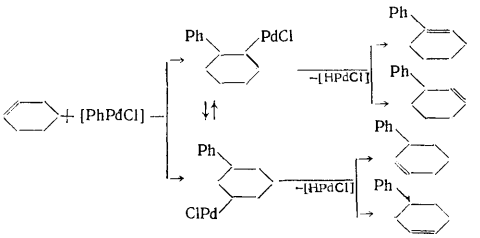
Alkene	Palladium compound	Solvent	*t*, °C	τ, h	Product	Yield, % calculated relative to the silane
Styrene	Li_2PdCl_4	THF	20	100	*trans*-stilbene	20**
Styrene	Li_2PdCl_4	THF	60	6	*trans*-stilbene	17
Styrene	Li_2PdCl_4	MeOH	60	6	*trans*-stilbene	20
Styrene	Li_2PdCl_4	THF	120	10	*trans*-stilbene	94
Styrene	$LiPdCl_3$	MeCN	120	10	*trans*-stilbene	65***
Styrene	Li_2PdCl_4	MeOH	120	10	*trans*-stilbene	47
Cyclohexene	Li_2PdCl_4	THF	120	10	phenylcyclohexane	35
Cyclohexene	$LiPdCl_3$	MeCN	120	10	1-phenylcyclohexene	23
Cyclohexene	Li_2PdCl_4	MeOH	120	10	phenylcyclohexane	38
					biphenyl	15

* Molar ratio $[Me_3SiPh] : [alkene] : [Pd^{II}] = 1 : 2 : 1$.
** + 5% β-methylstyrene.
*** + 8% β-methylstyrene.

Cyclohexane is phenylated less readily than styrene. The formation of 1-phenylcyclohexene, the "normal" product of the phenylation of cyclohexene, as the only product is observed only in acetonitrile. The reactions in THF and MeOH are complicated by side reactions—isomerisation, hydrogenation, and disproportionation:



Thus the reaction of Me_3SiPh with cyclohexene in the presence of Li_2PdCl_4 in the THF at 80°, in addition to the main product, 1-phenylcyclohexene, also gives 3- and 4-phenylcyclohexenes and phenylcyclohexane. The formation of the isomeric phenylcyclohexenes is attributed[60] to the isomerisation of the intermediate phenylcyclohexylpalladium chloride, since 1-phenylcyclohexenes do not isomerise under the reaction conditions:



At 120° in THF, the only product of the reaction of Me_3SiPh with cyclohexene is phenylcyclohexane. Under the same conditions in methanol, a mixture of phenylcyclohexane and biphenyl is formed. The formation of the latter is attributed to the disproportionation of 1-phenylcyclohexene under these conditions by a reaction of the irreversible Zelinskii catalysis type[60].

The above reactions involving the transfer of organic compounds to alkenes in the presence of Pd^{II} compounds are analogous to the familiar Heck reactions[41,72-76]. In the Heck reactions, organic derivatives of Hg, Sn, and Pb are used as alkylating and arylating agents.

The possibility of using organosilicon compounds in these reactions is of preparative interest, particularly for the methylation of alkenes, since organosilicon compounds are non-toxic and stable to air and moisture.

2. The Splitting of Silanes Under the Influence of Pt^{II} Compounds

Dimeric alkene complexes of Pt^{II} are active in the splitting of tetra-alkylsilanes[64-66].

The reactions of the silanes Me_3SiR (R = Ph, Me) with $Pt_2Cl_4(alkene)_2$ complexes take place even at room temperature. In $CHCl_3$ in the absence of water, the reaction gives Me_3SiCl and the corresponding σ-organic derivative of Pt^{II}, identified by ^1H NMR:

$$Me_3SiR + Pt_2Cl_4(C_2H_4)_2 \rightarrow Pt_2Cl_3(C_2H_4)_2R + Me_3SiCl .$$

In an excess of Me_3SiR, the reaction may proceed further:

$$Me_3SiR + Pt_2Cl_3(C_2H_4)_2R \rightarrow Pt_2Cl_2(C_2H_4)_2R_2 + Me_3SiCl .$$

The rate of the removal of different groups from the Si atom in Me_3SiR under the influence of $Pt_2Cl_4(C_2H_4)_2$ at 20° in $CHCl_3$ changes in the following order:

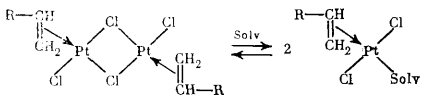
$$CH_2{=}CH > CH_2{=}CH{-}CH_2 > Ph \gg Me .$$

In the presence of water, the process becomes catalytic with respect to the Pt^{II} complex. As in reactions catalysed by Pd^{II} and Pt^{IV} complexes, the catalyst is regenerated by the protolytic splitting of the σ-organic derivative of the metal:

$$2Me_3SiCl + H_2O \rightarrow Me_3SiOSiMe_3 + 2HCl$$
$$[Pt_2Cl_3(C_2H_4)_2R_2] + 2HCl \rightarrow [Pt_2Cl_4(C_2H_4)_2] + 2RH .$$

In the reaction with Me_3SiPh, a wide range of monomeric *cis*- and *trans*-complexes of Pt^{II} containing phosphines, pyridines, biallyl, thiols, and ethene as ligands have been studied. All were inactive under the conditions studied (20°, 24 h). Among the dimeric complexes $Pt_2Cl_4L_2$, the collidine and phosphine complexes are also inert.

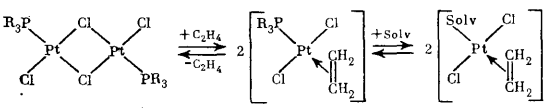
The high activity of dimeric alkene complexes of Pt^{II} in reactions with silanes was attributed[66] to the ease of formation of the intermediate coordinatively unsaturated Pt^{II} complex obtained by the dissociation of $Pt_2Cl_4(alkene)_2$:



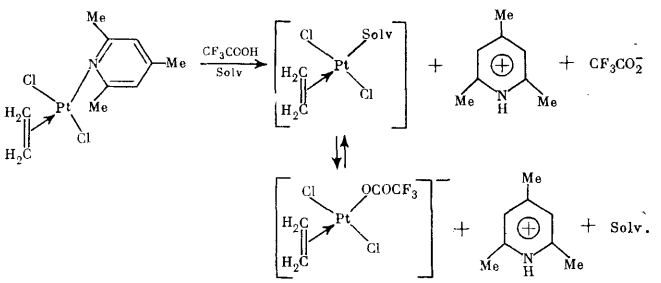
Solv = solvent .

In agreement with this, the rate of the splitting of silanes under the influence of the complexes $Pt_2Cl_4(C_2H_4)_2$ depends significantly on the solvent. Thus after 20 h, Ph is removed from Me_3SiPh to the extent of 100% in $CHCl_3$, 60% in benzene, 10% in acetone, and 2% in MeOH.[66] Thus solvents which form stable solvates decrease the coordinative unsaturation of the intermediate monomeric complex $PtCl_2(C_2H_4)$, and hinder the reaction.

The suggestion that an active three-coordinate Pt^{II} complex is formed agrees with the fact that the phosphine complexes $Pt_2Cl_4L_2$ [L = PPh_3 and $P(n\text{-}Bu)_3$], which are inert in reactions with silanes, react with them in the presence of ethene. The replacement of ethene by argon stops the reaction, and saturation again with ethene renews it. These facts are explained by ligand exchange in the presence of ethene.



Similarly, the ethene complex of Pt^{II} with the collidine ligand, *trans*-$PtCl_2(C_2H_4)(Me_3C_5H_2N)$, which is inactive in reactions with silanes, reacts with them in the presence of CF_3COOH at room temperature[64]. It has been proved that in the presence of CF_3COOH, protonation and removal of the collidine ligand take place to give the complex $PtCl_2(C_2H_4)$.



The unique activity of the complex $[PtCl_2(C_2H_4)Solv]$ is attributed to the increased electrophilic character of Pt^{II} in the presence of the π-acceptor, and the coordinative unsaturation of this complex.

The nature of the ethene ligand in the dimeric complex $Pt_2Cl_4(alkene)_2$ also influences its activity with respect to the Si-C bond. With increase in the size of the group R at the co-ordinated multiple bond, the rate of the splitting of silanes decreases in the order: ethene > styrene > propene > pentene > 3,3'-dimethyl-1-butene. This is attributed to the decrease in the accessibility of the metal with increase in the volume of the group R.

Low activity in the reaction with Me_3SiPh is also shown by the dimeric complex $Pt_2Cl_4(S\text{-}Bu_2\text{-}n)_2$, which has bridging ligands and can be converted into the three-coordinate complex $PtCl_2(S\text{-}Bu_2\text{-}n)$.

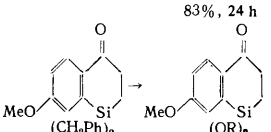
In the authors' opinion, Pt^{II} complexes can bring about either electrophilic splitting of the Si–C bond or oxidative addition of the silanes at the Si–C bond with the subsequent reductive elimination of R_3SiCl.[65]

3. The Splitting of the Si–C Bond by Metallic Pt and Pd

Metallic palladium in the presence of hydrogen is able to split the Si–CH_2Ph bond[77]. Thus various benzyl- and dibenzylsilanes in the presence of the catalytic complexes Pd/C in alcohol in an atmosphere of hydrogen are converted into alkoxysilanes and toluene. The reactions take place slowly at room temperature:

$$PhMe_2SiCH_2Ph \rightarrow PhMe_2SiOMe \quad (67\%,\ 24\ h)$$

$$m\text{-}MeOC_6H_4Si(Et)(CH_2Ph)_2 \rightarrow m\text{-}MeOC_6H_4Si(OEt)_2Et \quad (83\%,\ 24\ h)$$



54% (R = Me)
55% (R = Et)

$$C_6H_{11}Me_2SiCH_2Ph \rightarrow C_6H_{11}Me_2SiOMe \quad (10\%,\ 9\ d)$$

The method can be used to synthesise alkoxysilanes difficult to prepare, for example dialkoxysilatetralins. Electron-donor groups in the benzene ring facilitate the reaction, and acceptor groups (CF_3) hinder it. This feature led the authors to the conclusion that complex formation by the benzyl π-system with metallic Pd is the limiting stage of the process. The activated Si-benzyl bond is then split by alcohol (by an S_NSi mechanism) to give the alkoxysilane and benzylpalladium hydride, after which the latter is reduced by hydrogen to toluene and Pd^0. Platinum is inactive in this reaction. It has been shown, however, that the Si–Ph bond in Me_3SiPh is split very slowly under the influence of Pt/C in ethanol at 100°. The degree of conversion of the silane after 50 h corresponds to 32 moles per g-atom of platinum[62].

The triphenylphosphine complexes L_4Pt and L_4Pd are inert with respect to silanes on prolonged heating in benzene at 150°.[62] The apparent explanation is that the metal atom in these complexes is completely shielded, and is inaccessible to attack. The dissociation of L_4M gives the complexes L_3M and L_2M, in which the metal is still fairly well shielded by the molecules L and is still not readily accessible to attack by the silicon atom, which in turn is shielded by four organic groups[78].

4. Electrochemical splitting of the Si–C Bond.

Tetra-alkyl- and trialkylarylsilanes are oxidised at a Pt anode at 2.63 V in the presence of the fluoride anion in absolute MeCN.[79] The reaction is accompanied by the formation of fluorosilanes and the elimination of the most stable radical:

$$R_3SiR' \xrightarrow[H_3F_4^-,\ MeCN]{Pt,\ 2.63\ V} R_3SiF + R'^{\cdot} \quad (50\text{–}80\%)$$

R′ = Me, Et, CH_2Ph .

Silanes are not oxidised in the absence of the fluoride anion. In the authors' opinion, this reaction takes place by a mechanism involving one-electron oxidation with the nucleophilic co-operation of the fluoride anion. The transfer of the electron from Si takes place in step with the attack by F^- at the Si atom.

The proposed mechanism is confirmed by the selectivity of the splitting of the Si–C bonds and the nature of the products formed. Thus in the anodic oxidation of Me_3SiPh and $Me_3SiC_6H_4F$, the methyl group is eliminated exclusively, whereas in the case of trimethylbenzyl- and triethylbenzylsilanes, only the benzyl group is eliminated. The anodic oxidation of Me_3SiEt is accompanied by the preferential replacement of the ethyl group. Thus the ease of the removal of the radicals decreases in the order: $PhCH_2$ > Et > Me. The resulting radical then dimerises, or removes hydrogen from the solvent ($Me^{\cdot}$), or undergoes further anodic oxidation to the cation ($Et^{\cdot}$, $PhCH_2^{\cdot}$).

It is of interest to compare the selectivity of the splitting of the Si–C bond under the influence of Pd^{II} and Pt^{IV} on the one hand and in electrochemical splitting at a platinum anode on the other. In the first case, in trimethylarylsilanes, the aryl group is removed exclusively, whereas in the mixed trimethylethyl-, trimethylpropyl-, and trimethylbutylsilanes, practically only the methyl group is removed. Unlike the Ph and Me groups, the benzyl group is not removed from the Si atom under the influence of the complex $Pt_2(C_2H_4)_2Cl_4$. The opposite relationships are observed for the electrochemical oxidation of silanes.

5. The Reactions of Siloxanes with Platinum and Palladium Complexes

Of particular interest is the splitting of the silicon–oxygen bond in siloxanes, which would open up the possibility of using the readily accessible siloxanes in organic synthesis. On the other hand, the selectivity of the replacement of organic groups in siloxanes by polar groups provides a method for the directed modification of siloxanes in the absence of aggressive media.

The siloxane bond is fairly strong, and is split only by strong acidic and basic reagents[80]. There are several published examples, indicating the stability of siloxanes to the action of Pt and Pd complexes. Thus the reactions of substituted acetylenes with dihydrodisiloxanes in the presence of the Speier catalyst or Pt/C at 110° in toluene gives five-membered organocyclosiloxanes[81], that is, the reaction takes place without rupture of the SiOSi unit:

$$XC{\equiv}CX' + HR'RSiOSiRR'H \xrightarrow{catalyst} R'RSi\begin{matrix}O\\ \diagdown\ \diagup\\ XHC{-}CHX'\end{matrix}SiRR' \quad (50\text{–}70\%)$$

X = H, Ph; X′ = Ph;
R = R′ = Me; R = Me, R′ = Et .

When hexamethyldisiloxane is heated for a prolonged period with trichlorosilane at 150° in the presence of $H_2PtCl_6.6H_2O$, $PtCl_2$, or $Pt_2Cl_4(C_2H_4)_2$, selective exchange takes place between the methyl group and chlorine, and the siloxane bond is not affected[82]:

$$Me_3SiOSiMe_3 + HSiCl_3 \xrightarrow[150°,\ 24\ h]{catalyst} ClMe_2SiOSiMe_2Cl + HClSiMe_2 .$$

When 1,1,3,3-tetramethyldisiloxane is boiled with $L_2Pt(C_2H_4)$ in benzene, a disila-ring containing the metal is obtained[83]:

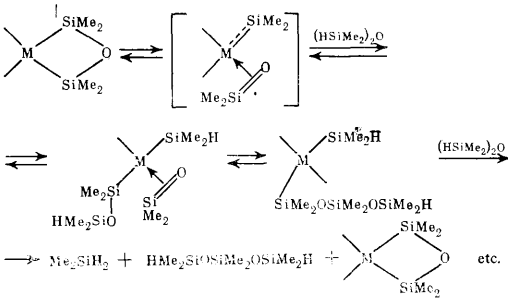
$$(HMe_2Si)_2O + L_2Pt(C_2H_4) \xrightarrow[C_6H_6]{20\text{–}80°} L_2Pt\begin{matrix}Me_2\\ Si\\ \diagup\ \ \diagdown\\ Si\\ Me_2\end{matrix}O + C_2H_4 + H_2$$

L = Ph_3P .

In this case, selective splitting of the Si–H bonds is observed, and rupture of the siloxane bond is not observed. The palladium, iridium, and rhodium analogues of these complexes were subsequently obtained[84]. Metal-containing rings of the type $L_2M(Me_2SiOSiMe_2)$ even at room temperature catalyse the disproportionation of 1,1,3,3-tetramethyldisiloxane to give dimethylsilane and higher siloxane oligomers:

$$n\,(HSiMe_2)_2O \xrightarrow{\text{catalyst}} Me_2SiH\,(OSiMe_2)_n\,OSiMe_2H + n\,Me_2SiH_2$$
$$M = Ir,\ Rh,\ Pt,\ Pd.$$

The platinum and palladium metal-containing rings are poor catalysts for these reactions, but the iridium and rhodium complexes show a high activity[84]. The authors suggest that the disproportionation of the disiloxane involves the participation of intermediate complexes of dimethylsilylene and dimethylsilanone, co-ordinated to the transition metal atom:



The dimeric ethene complex of platinum $Pt_2Cl_4(C_2H_4)_2$ in the presence of water brings about the slow hydrolysis of hexamethyldisiloxane at room temperature to give polysiloxanes[64]. The composition of the products was not determined.

It was noted above that the hydrosilylation of hex-2-ene under the influence of $(Me_3SiO)_2SiMeH$ at 140° in the presence of H_2PtCl_6 is complicated by a side process, which is also accompanied by the splitting of the siloxane bond[56]. The platinum and palladium compounds $PdCl_2$, $PtCl_4$, $H_2PtCl_6.6H_2O$, $(Ph_3P)_2PtCl_2$, $(Ph_3P)_4Pt$, and $(Ph_3P)_4Pd$, and also metallic Pt and Pd at 80–100°, activate both the Si–C bond and the Si–O bond in hexamethyldisiloxane. Linear and cyclic siloxanes are formed. The chief product is octamethyltrisiloxane, the yield of which corresponds to 10 moles per mole of catalyst[58, 60,61]. In the reaction of hexamethyldisiloxane with $PdCl_2$ (molar ratio 2:1, 150°, 10 h, in the absence of a solvent), methane, methyl chloride, and ethane are formed in the molar ratio 70:10:1 together with chlorine derivatives and higher linear and cyclic siloxanes[85].

In solvents (aqueous THF, MeCN, and MeOH), hexamethyldisiloxane reacts with Pd^{II} salts at 120° to give octamethyltrisiloxane, decamethyltetrasiloxane, and hexamethylcyclotrisiloxane. In the presence of $CuCl_2$, this reaction becomes catalytic. Thus 1 mole of Li_2PdCl_4 at 120° after 10 h converts approximately 5 moles of disiloxane. Metallic Pt and Pd are also active in the splitting, and the reaction with Pt/C takes place even at 80°. The products are methane and $Me_3SiOSiMe_2OSiMe_3$. The degree of conversion of the disiloxane after 10 h amounts to 10 mole per g-atom of Pt.[85]

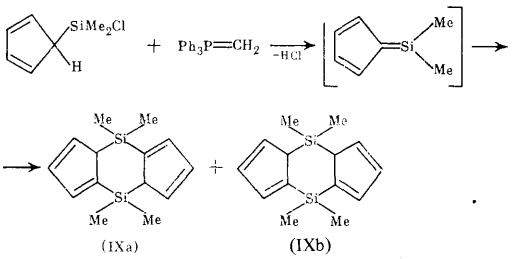
Unlike metallic platinum and palladium, the triphenylphosphine complexes of these metals, $(PPh_3)_4Pt$ and $(Ph_3P)_4Pd$, do not react with hexamethyldisiloxane in benzene even at 150°. The reaction with these complexes was observed only at 200°, that is under conditions in which decomposition of the complex to the metal is possible[85]. A significant feature is that the formation of cyclic siloxanes from hexamethyldisiloxane under the influence of platinum and palladium compounds or the corresponding metals is observed not only in aqueous solvents, but also under anhydrous conditions and in the initial stages of the reaction.

To explain the formation of cyclic dimethyldisiloxanes under anhydrous conditions, the authors assumed the intermediate formation of silacetone $Me_2Si=O$, stabilised by complex formation with a transition metal compound. Its polymerisation gives cyclic siloxanes, and insertion into linear and cyclic siloxanes at the Si–O bond gives higher linear and cyclic oligomers:

$$Me_3SiOSiMe_2OSiMe_3 + ML_n \rightleftarrows Me_3SiOSiMe_3 + Me_2SiO\cdot ML_n$$
$$Me_2SiO\cdot ML_n \xrightarrow{\text{polymerisation}} (Me_2SiO)_n$$
$$Me_2SiO\cdot ML_n \xrightarrow{Me_3Si(OSiMe_2)_n\,Me} Me_3Si\,(OSiMe_2)_{n+1}\,Me$$
$$Me_2SiO\cdot ML_n \xrightarrow{(Me_2SiO)_n} (Me_2SiO)_{n+1}.$$

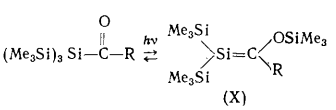
Until recently, it was considered that compounds containing a silicon atom forming multiple bonds did not exist. The formation of unstable organosilicon compounds with a double $(p-p)_\pi$-bond at the silicon atom is now well established. Thus the formation of short-lived silicon analogues of the unsaturated compounds $R_2Si=CH_2$,[86–90] $R_2Si=O$,[87,91] $R_2Si=SiR_2$,[92,93] $R_2Si=NR$,[94] and $R_2Si=S$[95] has now been proved.

Recently, several groups of research workers have attempted to synthesise stable silaethylenes. Thus with the idea of stabilising structures of the type C=E by delocalisation of the π-bond and an increase in the steric hindrance at the C and E atoms, attempts have been made[96] to synthesise silafulvenes, which, according to quantum-mechanical calculations[97], should be the most stable systems. The reaction of $C_5H_5SiMe_2Cl$ with triphenylmethylenephosphorane, however, instead of the expected silafulvene, gave a mixture of its dimers (IXa) and (IXb) with sp^3 hybridisation of the silicon atoms. The authors consider that the intermediate products of this reaction—silafulvenes—are too reactive, and are converted exceptionally readily into the thermodynamically stable dimers:



(IXa) (IXb)

Silaethylenes (X), relatively stable at room temperature in argon, were first obtained by the photolysis of acylpolysilanes[88]:



R=CMe$_3$, CEt$_3$, 1-adamantyl, etc.

With R = 1-adamantyl, a solid compound stable in argon, and characterised from its infrared, Raman, NMR (^1H, ^{13}C, ^{29}Si), and mass spectra, was isolated. Its structure (X) was confirmed by X-ray diffraction. Attempts to stabilise the intermediate unstable species of the silaethylene $R_2Si=CH_2$[98] and sila-allyl $R_2Si=CH=CH_2$[99–101] type by co-ordination to complexes of transition metals (Fe, Mo, W) has as yet, unfortunately, been unsuccessful.

Thus the new branch of metal-complex catalysis in organosilicon chemistry has arisen and developed successfully in the last ten years.

In this period it has been found that platinum and palladium complexes are effective catalysts for the splitting of Si–C bonds in vinyl-, allyl-, and ethynylsilanes, strained

sila- and disilacyclobutanes, silyl hydrides, and alkyl- and arylsilanes. These studies are being carried out with a view to investigating the mechanism of the activation of Si–C bonds by Pt and Pd complexes, and also using the splitting of these bonds in synthesis.

The removal of unsaturated groups from the Si atom is preceded by complex formation at the multiple bond. The driving force of the splitting of the Si–C bonds in cyclosilanes is their strain. In the splitting of Si–C bonds by Pd complexes, a significant feature is the ability of the Pd atom both to accept an electron pair from the carbon of the Si–C bond and to take part in a co-ordinative interaction with the silicon atom.

The splitting of Si–C bonds opens up new possibilities for the use of organosilicon compounds in synthesis: for the vinylation, methylation, phenylation, and chloroethylation of alkenes, the polymerisation of sila- and disilacyclobutanes, the preparation of organosilicon compounds not readily obtained, by the direct replacement of organic group on Si, the synthesis of platinum and palladium complexes containing organic and organosilicon groups on the metal, etc. The splitting of Si–C bonds in siloxanes is opening up new possibilities for the modification and oligomerisation of siloxanes.

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The Synthesis and Properties of Aliphatic Fluoronitroso-compounds

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The methods of synthesis and properties of aliphatic fluoronitroso-compounds are described systematically and the mechanisms of their reactions are discussed. A section is devoted to a survey of the properties and applications of copolymers of fluoronitroso-compounds.
The bibliography includes 304 references.

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I. INTRODUCTION

Compared with their non-fluorinated analogues, fluoronitroso-compounds are more electrophilic and the dissociation energy of their C–N bond is low, which led to the discovery of new reactions of both theoretical and practical importance—in particular the ready copolymerisation of fluoronitrosoalkanes with fluoro-olefins which leads to the formation of fluoronitroso-rubbers with unique properties.

This review includes data up to 1981 inclusive.

II. THE SYNTHESIS OF ALIPHATIC FLUORONITROSO-COMPOUNDS

The first representative of perfluoronitrosoalkanes, namely trifluoronitrosomethane, was obtained accidentally in 1936. Ruff and Giese[1] obtained trifluoronitrosomethane in a low yield by treating silver cyanide, containing an admixture of silver nitrate, with elemental fluorine. Interest in substances of this class was not renewed until the beginning of the 1950s when the chemistry of organofluorine substances began to develop vigorously. A series of general and special methods of synthesis, which have rendered available many aliphatic fluoronitroso-compounds, were also developed at that time.

1. Radical Reactions with Participation of Nitric Oxide

The first method of synthesis of trifluoronitrosomethane from trifluoroiodomethane and nitric oxide was proposed by Haszeldine[2]. Subsequently, this method was extended to a series of homologues of trifluoronitrosomethane[3–5]. It is based on the photochemical reaction of perfluoroalkyl iodides with nitric oxide in the presence of mercury as the acceptor of the evolved iodine:

$$R_F{-}I \xrightarrow{h\nu} \dot{R}_F + \dot{I}, \quad \dot{R}_F \xrightarrow{\dot{N}O} R_F{-}NO ,$$
$$2\dot{I} \xrightarrow{Hg} HgI_2 .$$

It is of interest that, when higher perfluoroalkyl iodides are used in this method in the absence of mercury, nitroso-compounds with a shorter fluorocarbon chain are formed in addition to the corresponding fluoronitroso-compounds[6,7]:

$$CF_3CF_2\dot{C}F_2 \xrightarrow{\dot{N}O} CF_3CF_2CF_2{-}NO; \quad 2NO \xrightarrow{h\nu} NO_2 + {}^1/_2\,N_2$$
$$CF_3CF_2\dot{C}F_2 \xrightarrow{NO_2} CF_3CF_2CF_2{-}ONO \xrightarrow[\dot{N}O]{h\nu} CF_3CF_2CF_2{-}\dot{O} \xrightarrow{O=CF_2}$$
$$\longrightarrow CF_3\dot{C}F_2 \xrightarrow{NO_2} CF_3CF_2{-}ONO \xrightarrow[\dot{N}O]{h\nu} CF_3CF_2{-}\dot{O} \xrightarrow{O=CF_2} \dot{C}F_3 .$$
$$\downarrow \dot{N}O \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \dot{N}O$$
$$CF_3CF_2{-}NO \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CF_3{-}NO$$

The purpose of mercury therefore consists not only in binding the iodine evolved but also in binding nitrogen dioxide, which appears on disproportionation of nitric oxide[7]. The yields of fluoronitrosoalkanes synthesised by this method are fairly high but the degree of conversion is low. It has also been shown that this reaction can occur on thermal initiation[8] but with a low yield.

Perfluoroalkyl bromides can also be introduced into this reaction[9]. Unsaturated fluoronitroso-compounds have likewise been obtained in this way[10,11]:

$$\begin{matrix} CF_2{=}CF{-}I \\ \\ CF_2{=}CX{-}CF_2{-}I \end{matrix} + NO \xrightarrow[Hg]{h\nu} \begin{matrix} CF_2{=}CF{-}NO \\ (9\%) \\ CF_2{=}CX{-}CF_2{-}NO \ ; \\ X{=}F\,(24.5\%);\ X{=}H\,(34\%) . \end{matrix}$$

Fluorodinitrosoalkanes can be synthesised by the radical reaction of fluoro-olefins with nitric oxides[303,304]:

$$CF_2{=}\underset{\displaystyle X}{\underset{|}{CF}} + 2NO \xrightarrow{\Delta,h\nu} ON{-}CF_2{-}\underset{\displaystyle X}{\underset{|}{CF}}{-}NO ;$$
$$X{=}F,\ Cl,\ CF_3 .$$

Several other methods, based on a different procedure for the generation of fluoroalkyl radicals and nitric oxide, were proposed later[12–16]:

$$CF_3COOH + Cl{-}NO\ (or\ BrNO) \xrightarrow[\text{gas phase}]{h\nu} CF_3{-}NO ;$$
$$CF_3{-}CF_3\ (or\ CF_3Cl) + NO \xrightarrow[12\ MH_2]{\text{chemical plasma}} CF_3{-}NO ;$$
$$(CF_3)_2C{=}O + 2NO \xrightarrow{h\nu} 2CF_3{-}NO ;$$
$$CF_3{-}H + Cl{-}NO \xrightarrow{h\nu,\Delta} CF_3{-}NO .$$

However, the need to work in the gas phase in a closed space in apparatus transparent to ultraviolet light lowers the value of this method for the synthesis of fluoronitroso-compounds in large amounts.

2. Decarboxylation of Perfluoroacyl Nitrites

Yet another method of synthesis of fluoronitrosoalkanes, based on the thermochemical and photochemical decarboxylation of perfluoroacyl nitrites, was proposed at the beginning

of the 1950s:

$$R_F—C—O—NO \xrightarrow[-CO_2]{\Delta(h\nu)} R_F—NO \ .$$

Several methods have been put forward for the thermal decomposition of perfluoroacyl nitrites. Direct heating[5,17–22] or contact with a high-boiling inert solvent[23–25] have been proposed to reduce the risk of explosion in the process.

A version of the decarboxylation of perfluoroacyl nitrites is their photochemical decomposition[26–30]. In certain cases perfluoroacyl nitrites decompose at the instant of formation[31]:

$$(CF_3)_3C—\overset{O}{\overset{\|}{C}}—F + Na—ONO \xrightarrow[-NaF]{} (CF_3)_3C—\overset{O}{\overset{\|}{C}}—ONO \xrightarrow[-CO_2]{} (CF_3)_3C—NO \ .$$

3. The Addition of Nitrosyl Fluoride to Fluoro-olefins

A method of synthesis of perfluoronitroso-compounds by the addition of nitrosyl fluoride to fluoro-olefins was developed in the 1960s. It was shown that, on passing from tetrafluoroethylene derivatives to higher fluoro-olefins, the mechanism of the addition of nitrosyl fluoride undergoes inversion[32]. Nitrosyl fluoride readily adds to tetrafluoroethylene via an electrophilic mechanism in the presence of boron trifluoride[32,33]:

$$F—NO + BF_3 \rightarrow BF_4^- + NO^+ \ ;$$

$$CF_2=CFX \xrightarrow{NO^+} \overset{+}{C}F_2—CFX—NO \xrightarrow[-BF_3]{BF_4^-} CF_3—CFX—NO \ ;$$

X=F, Cl .

When X = F, the nitroso-compound cannot be isolated, since it immediately gives rise to an oxazetidine on reaction with a second tetrafluoroethylene molecule:

$$CF_2=CF_2 + F—NO \xrightarrow{BF_3} CF_3—CF_2—N=O \xrightarrow{CF_2=CF_2} CF_3—CF_2—\underset{\displaystyle CF_2—CF_2}{\overset{\displaystyle |}{\overset{\displaystyle |}{N—O}}} \ .$$

Fluoronitrosyl compounds are formed via the same mechanism from alkyl perfluorovinyl ethers and nitrosyl fluoride[33–35]:

$$RO—CX=CF_2 \xrightarrow{NO^+} RO—\overset{+}{C}X—CF_2—NO \xrightarrow{F^-} RO—CXF—CF_2—NO \ ;$$

X=F, Cl, R_F .

Nitrosyl fluorides add to higher fluoro-olefins via a nucleophilic mechanism in the presence of fluoride ions[32,36,37]:

$$CF_3—\underset{\displaystyle X}{\overset{\displaystyle |}{C}}=CF_2 \xrightarrow{F^-} CF_3—\overset{-}{\underset{\displaystyle X}{\overset{\displaystyle |}{C}}}—CF_3 \xrightarrow[-F^-]{F—NO} (CF_3)_2C—\underset{\displaystyle X}{\overset{\displaystyle |}{N}}—O \ ;$$

X=F, CF_3 .

The possibility of a radical interaction of nitrosyl fluoride with tetrafluoroethylene to form difluorocarbene when the reaction is initiated by ultraviolet radiation has been postulated[40]:

$$F—NO + CF_2=CF_2 \xrightarrow{u.v.} \underset{(I)}{} \underset{\displaystyle CF_2}{\overset{\displaystyle CF_2—CF_2}{}} + \underset{(II)}{CF_3—\underset{\displaystyle CF_2—CF_2}{\overset{\displaystyle |}{\overset{\displaystyle |}{N—O}}}} + \underset{(III)}{CF_3—CF_2—\underset{\displaystyle CF_2—CF_2}{\overset{\displaystyle |}{\overset{\displaystyle |}{N—O}}}} \ ;$$

$$CF_2=CF_2 \xrightarrow{u.v.} 2\ddot{C}F_2 \ ;$$

$$\ddot{C}F_2 + F—NO \xrightarrow{u.v.} \dot{C}F_3 + \dot{N}O \longrightarrow CF_3—NO \xrightarrow{CF_2=CF_2} \Big\rfloor \rightarrow CF_3—\underset{\displaystyle CF_2—CF_2}{\overset{\displaystyle |}{\overset{\displaystyle |}{N—O}}} \ ;$$

$$CF_2=CF_2 + F—NO \xrightarrow{u.v.} F—\underset{\displaystyle CF_2—CF_2}{\overset{\displaystyle |}{\overset{\displaystyle |}{N—O}}} \xrightarrow{\ddot{C}F_2} \dot{C}F_3 + \dot{N}—\underset{\displaystyle CF_2—CF_2}{\overset{\displaystyle |}{\overset{\displaystyle |}{O—}}} \Big\rfloor$$

(III)

$$CF_2=CF_2 + \ddot{C}F_2 \rightarrow \underset{\displaystyle CF_2}{\overset{\displaystyle CF_2—CF_2}{}} \ .$$

(II)

The following facts have been adduced in support of the mechanism. In the absence of ultraviolet radiation, only compound (IV) is formed:

$$CF_2=CF_2 + F—NO \rightarrow CF_3—CF_2—NO \xrightarrow{CF_2=CF_2} CF_3—CF_2—\underset{\displaystyle CF_2—CF_2}{\overset{\displaystyle |}{\overset{\displaystyle |}{N—O}}} \ .$$

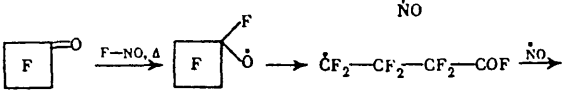
(IV)

When a mixture of compound (I), (II), and (IV) is irradiated, compound (III) is produced in a low yield.

There have been a number of other studies[36,37,41] in which it was shown that nitrosyl fluoride adds to fluoro-olefins also in the absence of a catalyst but at temperatures above 100 °C, which lowers the yield of fluoronitroalkanes due to side reactions.

Nitrosyl fluoride adds not only to fluoro-olefins but also to other compounds with a double bond[42,43]:

$$CF_2=C(CF_3)—COF \xrightarrow{F—NO} CF_3—\underset{\displaystyle NO}{\overset{\displaystyle |}{C}}(CF_3)—COF$$



$$\xrightarrow{F—NO,\ \Delta}$$

$$\rightarrow \dot{C}F_2—CF_2—CF_2—COF \xrightarrow{\dot{N}O} \rightarrow ON—CF_2—CF_2—CF_2—COF \ .$$

4. The Addition of Nitrosyl Chloride to Fluoro-Olefins

The first attempt to add nitrosyl chloride to fluoro-olefins[44–46] led only to the formation of nitroso-compounds. However, subsequently, using Lewis acids as catalysts, it was possible to obtain chlorofluoronitroso-compounds in both liquid[47] (without irradiation) and gaseous[48–50] (with and without irradiation) phases:

$$\left.\begin{array}{l} CF_2=CF_2 + Cl—NO \xrightarrow[\text{liq. phase}]{AlCl_3} \\ CF_2=CF_2 + Cl—NO \xrightarrow[\text{gas phase}]{h\nu, FeCl_3} \end{array}\right\rfloor \rightarrow Cl—CF_2—CF_2—NO \xleftarrow[\text{gas phase}]{FeCl_3} NO + CF_2=CF_2 \ ;$$

$$FeCl_3 + NO \rightleftarrows FeCl_3NO \xrightarrow{NO} FeCl_2NO + Cl—NO \xrightarrow{FeCl_3} FeCl_4NO \xrightarrow{2NO} \rightarrow FeCl_2NO + 2Cl—NO$$

$$CF_3—S—CF=CF_2 + Cl—NO \xrightarrow[\text{gas phase}]{h\nu} CF_3—S—\underset{\displaystyle NO}{\overset{\displaystyle |}{C}}F—CF_2Cl \ .$$

Nitrosyl chloride adds smoothly to fluoro-olefins in the presence of potassium fluoride[39,77]:

$$X—CF=C(CF_3)_2 \xrightarrow[-KCl]{KF,\ Cl—NO} X—CF_2—C(CF_3)_2—NO \ ;$$

X=F, C_2F_5 .

Fluoronitrosoalkanes can be obtained by the reaction of nitrosyl chloride with organofluorine derivatives of mercury[51] and also with 1-hydro-1-fluorosulphonyltetrafluoroethane[76]:

$$(CF_3—CXY)_2Hg + Cl—NO \xrightarrow{-HgCl_2} 2CF_3—CXY—NO \ ;$$

$$\begin{matrix} FSO_2 \\ CF_3 \end{matrix}\!\!>\!CFH \xrightarrow[-H^+]{\text{pyridine}} \begin{matrix} FSO_2 \\ CF_3 \end{matrix}\!\!>\!\overset{-}{C}F \xrightarrow[-Cl^-]{Cl—NO} \begin{matrix} FSO_2 \\ CF_3 \end{matrix}\!\!>\!CF—NO \ .$$

5. The Interaction of Nitrogen Oxides with Fluoro-olefins

It has been observed[52,53] that tetrafluoroethylene readily combines with nitrogen dioxide. Apart from a dinitroalkane and a nitronitrite, a small amount of a nitronitrosoalkane is formed under these conditions[53]:

$$CF_2=CF_2 + N_2O_4 \rightarrow O_2N—CF_2CF_2—NO_2 + O_2N—CF_2CF_2—ONO + O_2N—CF_2CF_2—NO \ .$$

When nitric oxide is used, the yield of the nitronitrosoalkane is higher[54–58]. As a consequence of its low reactivity, pure nitric oxide does not react with fluoro-olefins in the

dark[59]. However, on irradiation nitric oxide disproportionates with formation of nitrogen dioxide and trioxide, which initiate the subsequent radical processes.

The addition of nitric oxide to fluoro-olefins can be initiated also by adding chlorine, bromine[55], and oxygen[57]. When nitrogen oxides interact with fluoro-olefins, the NO_2 radical, which initiates the process, attacks specifically the least sterically hindered difluoromethylene group[60-66]. Whereas the interaction of perfluoropropene with nitrogen oxides[56,60,65,66] results in the formation of a small amount of a dinitroalkane in addition to the nitronitrosoalkane and the nitronitrite, in the case of perfluoroisobutene a dinitroalkane is not formed[62,63]:

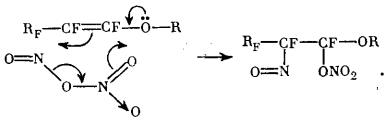
$$CF_3-CF=CF_2 \xrightarrow{N_2O_4} CF_3-\underset{NO}{CF}-CF_2-NO_2 + CF_3-\underset{ONO}{CF}-CF_2-NO_2 + CF_3-\underset{NO_2}{CF}-CF_2-NO_2 ;$$

$$(CF_3)_2C=CF_2 \xrightarrow{N_2O_4} (CF_3)_2\underset{ONO}{C}-CF_2-NO_2 + (CF_3)_2\underset{ONO}{C}-CF_2-ONO .$$

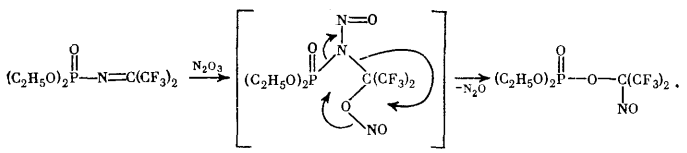
The interaction of perfluoroisobutene with nitrogen tetroxide in the presence of potassium fluoride leads to the formation of perfluoronitroso-t-butane alone[32,38]:

$$(CF_3)_2C=CF_2 \xrightarrow{F^-} (CF_3)_3C^- \xrightarrow{N_2O_4} (CF_3)_3C-N=O + NO_3^- .$$

Nitrogen dioxide adds to alkyl perfluorovinyl ethers[67] with formation of fluoronitrosonitrates:



Fluoronitrosoalkanes can also be formed by the reaction of phosphorylated imines with nitrogen trioxide[68]:



6. The Synthesis of Fluoronitro-compounds from Fluorine-containing Oximes

After the development of methods of synthesis of fluorooximes, fluoronitrosoalkanes were obtained by the Pilotti reaction[69,70]:

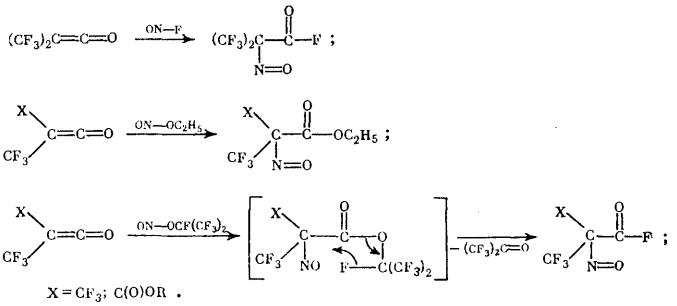
$$R_F-CF=N-OH \xrightarrow{Cl_2} \left[R_F-\underset{Cl}{CF}-\underset{Cl}{N}-OH\right] \xrightarrow{-HCl} R_F-CFCl-NO .$$

Perfluoro-2-nitrosopropane has been obtained by oxidising hexafluoroacetone oxime in anhydrous hydrogen fluoride[71]:

$$(CF_3)_2C=N-OH \xrightarrow[-H_2O]{Cr_2O_3,\ HF} (CF_3)_2CF-NO .$$

7. The Addition of Nitrosyl Fluoride and Alkyl Nitrites to Ketens

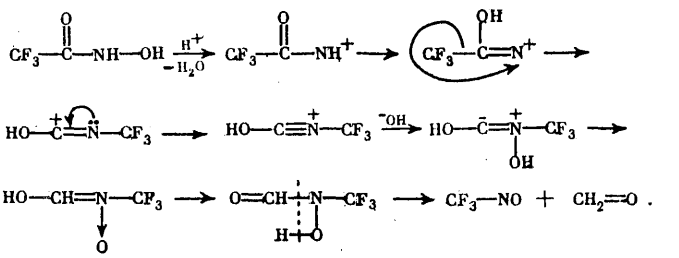
Derivatives of carboxylic fluoro-α-nitrosoacids can be obtained by the addition of nitrosyl fluoride and alkyl nitrites to ketens[72-75]:



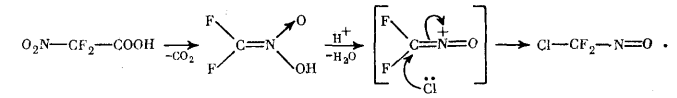
X = CF_3; C(O)OR .

8. Other Methods of Synthesis of Fluoronitroso-compounds

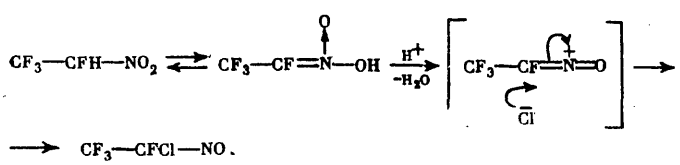
When trifluoroacetohydroxamic acid was heated *in vacuo*, trifluoronitrosomethane was obtained[79]. The following reaction mechanism is possible:



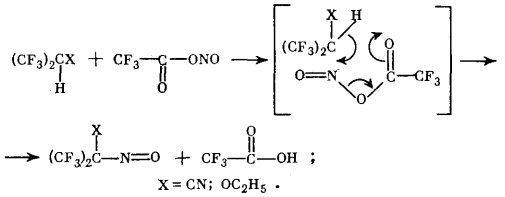
Difluoronitroacetic acid is converted into chlorodifluoronitrosomethane via several stages in a hydrochloric acid medium[80]:



When tetrafluoro-α-hydronitroethane was allowed to react with hydrogen chloride, the corresponding nitroso-compound was obtained[81]:

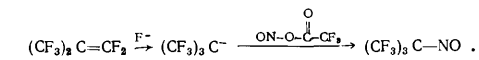


Derivatives of hexafluoro-2-nitrosoisobutyric acid can be obtained by the substitution of the hydrogen atom in the corresponding C–H acid by the nitroso-group on treatment with trifluoroacetyl nitrite[78]:



X = CN; OC_2H_5 .

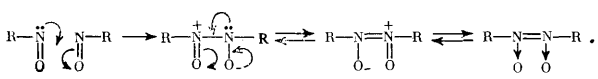
Trifluoroacetyl nitrite can also be used to synthesise fluoronitrosoalkanes from fluoro-olefins[78]:



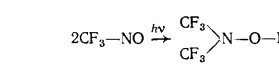
III. THE PROPERTIES OF ALIPHATIC FLUORONITROSO-COMPOUNDS

1. Characteristic Features of the Chemical Properties of Fluoronitrosoalkanes

A tendency towards dimerisation is a characteristic feature of non-fluorinated aliphatic nitroso-compounds[82,83] and most of them can exist in a monomeric form only in the melt, in solution, or in the gas phase[84]:



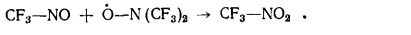
As a consequence of the decrease of the basicity of the nitrogen atom in fluoronitroso-compounds, the latter do not dimerise and they all exist exclusively in the monomeric form[84]. However, fluoronitrosoalkanes are also capable of forming dimers on irradiation but with a different structure[85]:

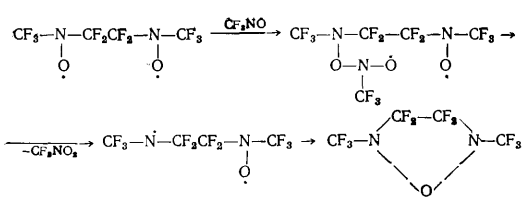


The inductive effect of the perfluoroalkyl group increases the electrophilicity of fluoronitrosoalkanes and decreases the C–N bond strength. Compared with their non-fluorinated analogues, fluoronitroso-compounds are therefore more readily reduced, are oxidised with greater difficulty, and typically undergo reactions with nucleophiles and reactions involving the dissociation of the C–N bond. In cycloaddition reactions fluoronitroso-compounds behave as active dienophiles.

2. Oxidation of Fluoronitroso-compounds

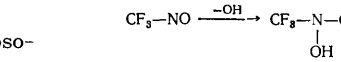
Trifluoronitrosomethane is a strong electrophile and is resistant to the action of oxidants (HNO_3, $HMnO_4$, $H_2Cr_2O_7$, and Hal_2).[86,87] The oxidation of perfluoronitrosoalkanes at 65–130 °C with hydrogen peroxide[5,7,88] and higher metal oxides[4,45] has been described. In the presence of Hopcalite trifluoronitrosomethane is oxidised only at 150–200 °C;[86] nitroxy-radicals are also capable of oxidising trifluoronitrosomethane[89,139]:





The most convenient method involves oxidation by liquid nitrogen tetroxide. Secondary fluoronitroso-compounds are then oxidised preferentially to nitro-compounds[76,90–92].

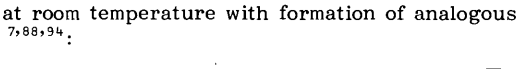
Tertiary fluoronitroso-compounds are oxidised by nitrogen tetroxide and other oxidants only to nitrites[38,39,42,62,90,93]:



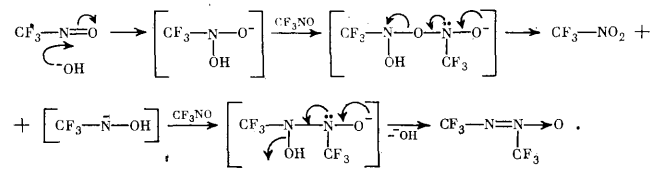
The formation of nitrites can be explained by the ready radical dissociation of the C–N bond in tertiary fluoronitroso-compounds.

3. Disproportionation of Fluoronitroso-compounds

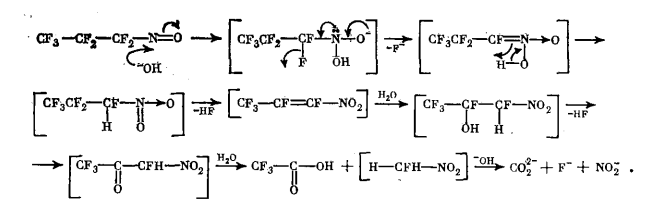
Fluoronitrosoalkanes, including trifluoronitrosomethane, undergo oxidative-reductive disproportionation over activated charcoal (at 100 °C) to perfluoronitroalkanes and perfluoroazoxyalkanes[7,88,94]:



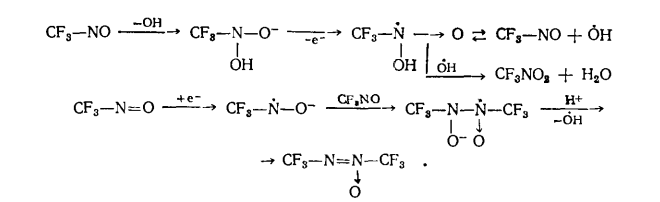
In aqueous alkalis trifluoronitrosomethane disproportionates at room temperature with formation of analogous products[7,88,94]:



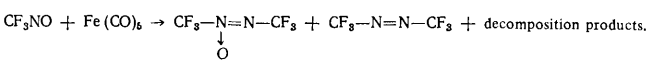
Higher homologues then decompose with formation of carboxylic acids[7,86,87]:



The radical-ion mechanism has also been proposed for the alkaline disproportionation of trifluoronitrosomethane[95] on the basis of EPR data:

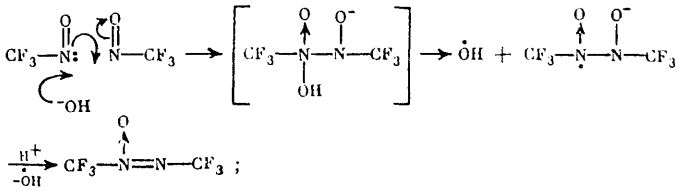


Hexafluoroazoxymethane is also formed when trifluoronitrosomethane reacts with iron pentacarbonyl[96]:



The preferential formation (90%) of hexafluoroazoxymethane in the presence of reducing agents (sodium hypophosphite—$NaHPO_3$) and the preferential formation (90%) of trifluoronitromethane in the presence of oxidising agents (sodium hypochlorite—NaOCl) [86] can be explained by means of a mechanism based on the hypothesis that charge-transfer

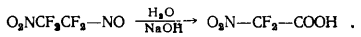
complexes are formed[97]:



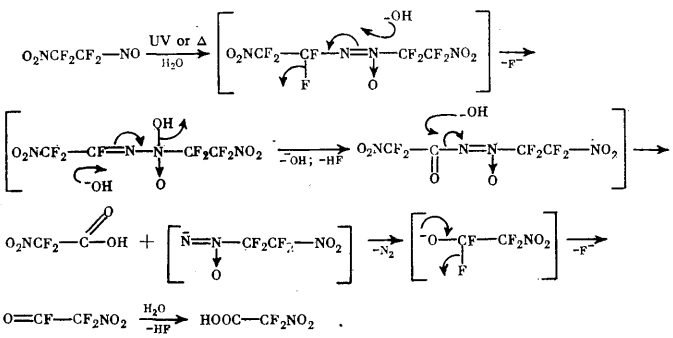
According to the authors, the reducing agent ($NaHPO_3$) binds hydroxy-radicals and prevents the formation of trifluoronitromethane, while the oxidising agent NaOCl generates hydroxy-radicals and promotes the preferential formation of trifluoronitromethane:

$$NaHPO_3 + 2\dot{O}H \rightarrow Na_2HPO_4 + H_2O \ ;$$
$$NaOCl + H_2O \rightarrow NaCl + 2\dot{O}H \ .$$

Tetrafluoro-2-nitro-1-nitrosoethane[98] hydrolyses to difluoronitroacetic acid in the presence of alkali:

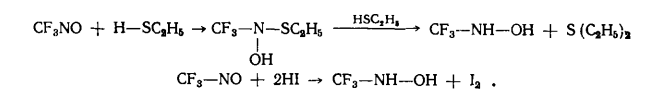


It is believed[98] that difluoronitroacetic acid is also formed in an aqueous medium on ultraviolet irradiation or on heating, via the intermediate formation of an azoxy-compound:

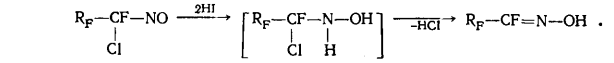


4. Reduction of Fluoronitroso-compounds

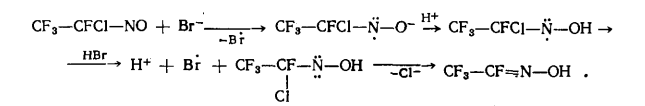
Trifluoronitrosomethane is reduced by ethanethiol and hydrogen iodide[86] to trifluorohydroxylamine, which is stable in the form of the etherate:



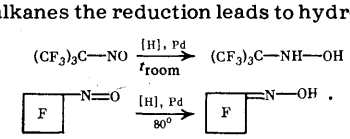
On reduction to hydroxylamine, α-chloroperfluoronitrosoalkanes[55,59] split off hydrogen halide with formation of the fluorides of perfluorohydroxamic acids:



Fluoronitrosoalkanes can be reduced also by other methods—by treating a solution of a nitrosoalkane and phenol in ether with bromine and by catalytic hydrogenation. In the former case the reducing agent is the bromide ion formed when bromine interacts with phenol[99]:



In the catalytic hydrogenation of secondary and tertiary fluoronitrosoalkanes the reduction leads to hydroxylamines[92,100]:



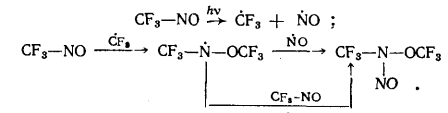
The attempts to reduce perfluoronitroso-t-butane to perfluoro-t-butylamine by hydrogenation over Raney nickel led only to the formation of perfluoromonohydro-t-butane—the product of the hydrogenolysis of the initial nitroso-compound. This finding confirms yet again the low energy of the C–N bond in tertiary fluoronitroso-compounds.

Perfluoro-t-butylhydroxylamine has been obtained in the form of the etherate by treating perfluoronitroso-t-butane with tin dichloride[101].

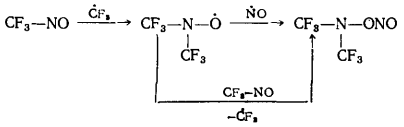
5. Pyrolysis and Photolysis of Fluoronitroso-compounds

The pyrolysis and photolysis of fluoronitroso-compounds proceed with dissociation of the C–N bond whose strength in trifluoronitrosomethane corresponds to 31–50 kcal mole^{-1} [102–106].

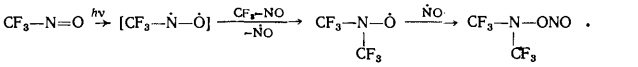
It has been suggested that in the photolysis of trifluoronitrosomethane the trifluoromethyl radical attacks the oxygen atom of the molecule of the nitroso-compound with [subsequent] formation of an *N*-nitroso-compound whose structure proved to be erroneous[107]:



A mechanism involving the attack of the nitrogen atom by the trifluoromethyl radical with formation of an *N*-nitrite, whose structure was demonstrated, was proposed later[108–109]:

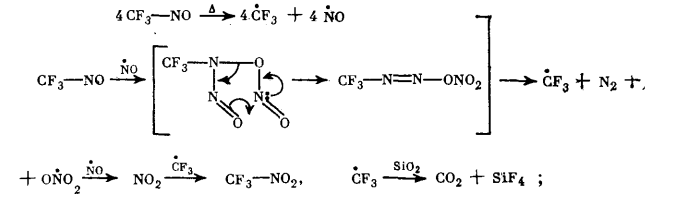


Masson[103] suggested that another primary step is also possible, in which the trifluoronitrosomethane molecule passes to an excited triplet state:



Since *N*,*N*-difluoro(trifluoromethyl)amine (CF_3NF_2) was not found among the products obtained on irradiation of trifluoronitrosomethane in the presence of tetrafluorohydrazine (N_2F_4), it was also concluded that there is no primary photodissociation of the C–N bond[110].

Thermal decomposition of trifluoronitrosomethane results in the formation of only trifluoronitromethane and low-molecular-weight decomposition products[111]. The following mechanism has been proposed to explain this:



or overall:

$$4CF_3{-}NO \xrightarrow{\Delta} 2CF_3{-}NO_2 + N_2 + 2\dot{C}F_3 \text{ (in the form of } CO_2 + SiF_4) .$$

Apart from trifluoronitromethane, tris(trifluoromethyl)-hydroxylamine and a polymeric product $(-CF_2{-}NF-)_n$ were isolated from the products of the pyrolysis of trifluoro-nitrosomethane at 250–300 °C:[112]

$$CF_3{-}NO \xrightarrow{250-300^\circ} \begin{cases} \longrightarrow \dot{N}O + \dot{C}F_3 \xrightarrow{CF_3NO} CF_3{-}\underset{CF_3}{N}{-}\dot{O} \xrightarrow{\dot{C}F_3} CF_3{-}\underset{CF_3}{N}{-}OCF_3 \\ \xrightarrow{CF_3NO} CF_3{-}NO_2 + [CF_3{-}\ddot{N}] \rightarrow CF_2{=}NF \rightarrow (-CF_2{-}NF-)_n . \end{cases}$$

On pyrolysis, higher homologues of trifluoronitrosomethane give rise to fluoroazomethines together with nitroalkanes[41,55,112,113]. Two mechanisms have been proposed to account for this finding[41,112]:

$$\text{a) } R_F{-}CF_2{-}NO \xrightarrow{\Delta} R_F\dot{C}F_2 + \dot{N}O ;$$

$$R_FCF_2{-}NO \xrightarrow{R_F\dot{C}F_2} R_FCF_2{-}\underset{\dot{O}}{N}{-}CF_2R_F \rightarrow R_F{-}CF{=}N{-}CF_2R_F +$$

$$+ \dot{O}F \xrightarrow{R_F\dot{C}F_2NO} R_FCF_2{-}NO_2 + \dot{F} \xrightarrow{R_F\dot{C}F_2} R_F{-}CF_3 ;$$

$$\text{(b) } (CF_3)_2CF{-}NO \xrightarrow{\Delta} (CF_3)_2\dot{C}F + \dot{N}O$$

$$(CF_3)_2CF{-}NO \xrightarrow{(CF_3)_2\dot{C}F} (CF_3)_2CF{-}\underset{\dot{O}}{N}{-}CF(CF_3)_2 \xrightarrow{\dot{N}O} (CF_3)_2CF{-}\underset{ONO}{N}{-}CF(CF_3)_2 \rightarrow$$

$$\rightarrow (CF_3)_2CF{-}\dot{N}{-}CF(CF_3)_2 + \dot{O}NO \rightleftarrows \dot{N}O_2$$

$$\xrightarrow[-RF]{\downarrow \dot{R}} (CF_3)_2C{=}N{-}CF(CF_3)_2 \qquad \xrightarrow{\downarrow (CF_3)_2\dot{C}F} (CF_3)_2CF{-}ONO \qquad \xrightarrow{\downarrow (CF_3)_2\dot{C}F} (CF_3)_2CF{-}NO_2$$

$$(CF_3)_2C{=}\dot{O} + F{-}NO ;$$

$\dot{R}$ = iso-$\dot{C}_3F_7$, $\dot{N}O$, $\dot{N}O_2$.

The first mechanism[112] gives rise to major doubts. It was shown later that trifluoronitrosomethane can produce on pyrolysis not only fluoroazomethines, like its higher homologues, but also hexafluoroazomethane[114]:

$$2CF_3{-}NO \longrightarrow CF_3{-}\underset{CF_3}{N}{-}ONO \longrightarrow CF_3{-}N{=}CF_2 + F{-}NO_2$$

$$\xrightarrow{SiO_2} NO_2 + SiF_4;$$

$$2CF_3{-}NO \longrightarrow \begin{matrix} CF_3{-}N{-}\dot{O} \\ | \\ CF_3{-}N{-}\dot{O} \end{matrix} \xrightarrow{2CF_3NO} \begin{matrix} CF_3 \\ | \\ CF_3{-}N{-}O{-}N{-}\dot{O} \\ | \\ CF_3{-}N{-}O{-}N{-}\dot{O} \\ | \\ CF_3 \end{matrix} \longrightarrow$$

$$\longrightarrow CF_3{-}N{=}N{-}CF_3 + 2CF_3NO_2;$$

$$CF_3{-}NO \xrightarrow{2NO} \begin{matrix} CF_3{-}N{-}O \\ | \quad | \\ N \quad N \\ \| \quad \| \\ O \quad O \end{matrix} \longrightarrow CF_3{-}N{=}N{-}ONO_2$$

$$\xrightarrow[-\dot{O}NO_2]{} CF_3{-}N{=}\dot{N} \xrightarrow{\dot{C}F_3} CF_3N{=}NCF_3.$$

On the basis of these data, it was concluded that trifluoro-nitrosomethane can be pyrolysed via the "diazonium nitrate",[111] via the dimer $(CF_3)_2N{-}ONO$,[108] and via the Andreades mechanism[41]. On thermal decomposition of α-chlorofluoronitroso-compounds[48,115], the products of the substitution of the nitroso-group by a chlorine atom were isolated together with nitroso-compounds:

$$ClCF_2{-}CFCl{-}NO \xrightarrow{\Delta} ClCF_2{-}\dot{C}FCl + \dot{N}O ;$$

$$ClCF_2{-}CFCl{-}NO \xrightarrow{\dot{N}O} ClCF_2{-}CFCl{-}NO_2 + {}^1/_2 N_2 ;$$

$$ClCF_2{-}\underset{Cl}{CF}{-}NO \xrightarrow{ClCF_2{-}\dot{C}FCl} [ClCF_2{-}\dot{C}F{-}NO] + ClCF_2{-}CFCl_2 .$$

A study has been published recently[116] in which the compositions of the pyrolysis and photolysis products of perfluoronitrosopropane were compared. Photolysis results in a more complex mixture of decomposition products:

$$C_3F_7{-}NO \xrightarrow[24\ h]{80^\circ} \underset{(72\%)}{C_3F_7{-}N{=}CF{-}C_2F_5} + \underset{(11\%)}{C_3F_7{-}NO_2} + \underset{(7\%)}{(C_3F_7)_2N{-}OC_3F_7} ;$$

$$C_3F_7{-}NO \xrightarrow[18\ h]{u.v.} \left.\begin{matrix} (C_3F_7)_2N{-}ONO \\ (C_3F_7)_2N{-}NO_2 \end{matrix}\right\} (30\%) + \begin{matrix} (C_3F_7)_2N{-}OC_3F_7 \\ (<30\%) \\ (C_3F_7)_2N{-}C_3F_7 \\ (<30\%) \\ (C_3F_7)_2N{-}N(C_3F_7)_2 \\ (<30\%) \end{matrix} .$$

In the catalytic fluorination of trifluoronitrosomethane[117] there is also a possibility of radical decomposition processes:

$$CF_3{-}NO \xrightarrow{F_2} CF_3{-}\underset{CF_3}{N}{-}OCF_3 + CF_3{-}\underset{F}{N}{-}OCF_3 .$$

An increase of the decomposition temperature of trifluoro-nitrosomethane from 30° to 170 °C in the presence of silver difluoride and of silver difluoride with a simultaneous supply of fluorine increases the yield of tris(trifluoromethyl)-hydroxylamine from 0 to 15% in the former case and reduces the yield from 55 to 7% in the latter case[118]:

$$CF_3{-}NO \xrightarrow{AgF_2} (CF_3)_2N{-}OCF_3 \xleftarrow[F_2]{AgF_2} CF_3{-}NO .$$

6. Interaction of Fluoronitroso-compounds with Radicals

(a) Interaction with Nitric Oxide

Trifluoronitrosomethane reacts with liquid nitric oxide[111] even at −100 °C with formation of trifluoronitromethane, *N*-bis(trifluoromethyl)ammonium nitrite, and nitrogen. In the gas phase the same products are formed much more slowly. A mechanism has been proposed with the intermediate formation of "diazonium nitrate":[111]

$$CF_3{-}NO \xrightarrow{2NO} \left[CF_3{-}\underset{N}{\overset{O}{N}} \longrightarrow CF_3{-}N{=}N{-}ONO_2 \right] \longrightarrow$$

$$\longrightarrow \dot{C}F_3 + N_2 + \dot{O}NO_2 \xrightarrow{\dot{N}O} 2\dot{N}O_2;$$

$$\dot{C}F_3 + \dot{N}O_2 \longrightarrow CF_3{-}NO_2;$$

$$CF_3{-}NO \xrightarrow{\dot{C}F_3} (CF_3)_2N{-}\dot{O} \xrightarrow{\dot{N}O} (CF_3)_2N{-}ONO;$$

or overall:

$$3CF_3NO + 3NO \rightarrow CF_3NO_2 + (CF_3)_2N{-}ONO + NO_2 + N_2.$$

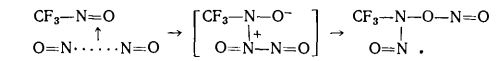
Later it was possible to detect the intermediate adduct of two nitric oxide molecules with a trifluoronitrosomethane molecule[119]:

$$CF_3{-}NO + 2NO \xrightarrow{-100^\circ} CF_3{-}\underset{N}{\overset{O}{N}} \xrightarrow{-50^\circ} \dot{C}F_3 + N_2 + \dot{O}NO_2 ;$$

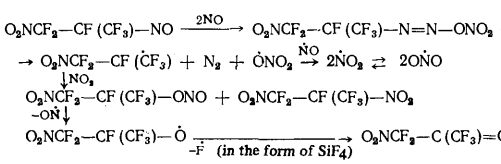
$$CF_3{-}NO + 2NO \xrightarrow{-100^\circ} CF_3{-}\underset{N}{\overset{O}{N}} \xrightarrow[CH_3ONa]{} CF_3{-}\underset{N}{N}{-}ONa + CH_3O{-}NO$$

$$CF_3{-}\underset{N}{\overset{O}{N}} \xrightarrow{2HN(C_2H_5)_2} CF_3{-}\underset{N}{N}{-}OH \cdot HN(C_2H_5)_2 + ON{-}N(C_2H_5)_2 .$$

Ginsburg et al.[119] claim reasonably that nitric oxide cannot attack trifluoronitrosomethane via a radical mechanism, since radical species were not detected by EPR at temperatures corresponding to the formation of the colourless adduct. A different pathway leading to the formation of this adduct was therefore proposed—via a complex of the trifluoronitrosomethane molecule with two nitric oxide molecules, which is stabilised as a result of electron transfer within the complex without the liberation of free radicals:

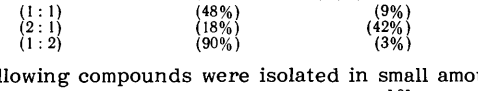


Apart from the dinitro-compound, an α-nitroketone is formed on interaction of 1-nitro-2-nitrosoperfluoropropane with nitric oxide[65]:

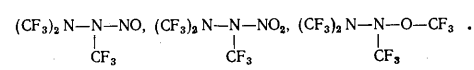


(b) Interaction with Fluoroalkyl and Other Radicals

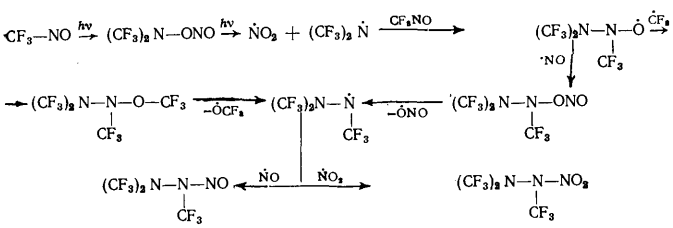
When trifluoronitrosomethane reacted with the trifluoromethyl radical, generated photochemically from trifluoroiodomethane[120,121], *N*-bis(trifluoromethyl)ammonium nitrite and tris(trifluoromethyl)hydroxylamine were obtained. The ratio of the initial reactants does not influence the ratio of the reaction products:



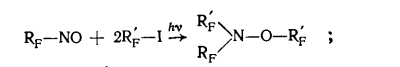
The following compounds were isolated in small amounts from the mixture of products of this reaction[121]:



In order to explain their formation, the mechanism

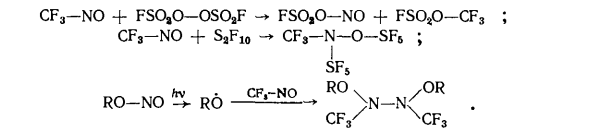


was put forward. Analogous reactions lead to both homogeneous and mixed hydroxylamines[113,122]:



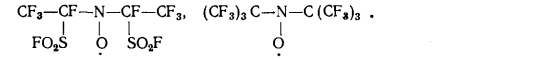
A number of studies have been devoted to the interaction of trifluoronitrosomethane with the trifluoromethyl radical, generated in different ways—by the pyrolysis of trifluoroacetyl nitrite[123], by the photolysis of hexafluoroazomethane[124], and by the photolysis of hexafluoroacetone[15].

Trifluoronitrosomethane reacts also with other substances which are readily converted into radicals[125–127]:

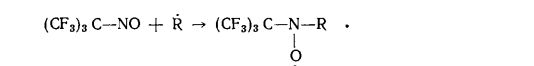


(c) Fluoronitroso-compounds as Radical-trapping Agents

On interaction with radicals, certain fluoronitrosoalkanes form relatively long-lived nitroxy-radicals which can be detected by EPR:[128,129]

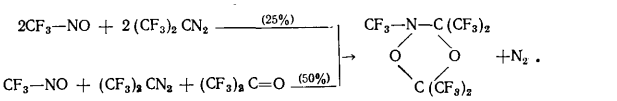


By virtue of this property, perfluoronitroso-t-butane has found applications[129–132] as a spin-trapping agent for long-lived radicals:



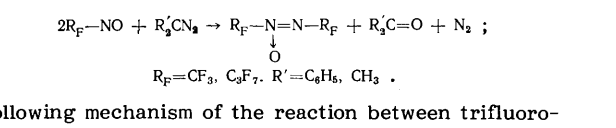
(d) Interaction With Carbenes

On interaction with bis(trifluoromethyl)azomethane, trifluoronitrosomethane gives rise to a cyclic product[133]:

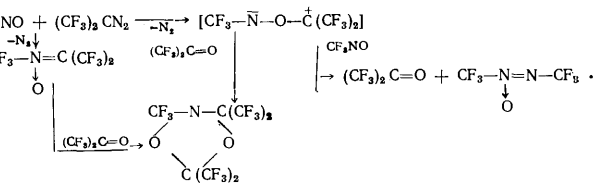


The authors suggested that hexafluoroacetone is formed as an intermediate, because the yield of the dioxazolidine increases by a factor of two when hexafluoroacetone is added to a mixture of trifluoronitrosomethane and bis(trifluoromethyl)diazomethane.

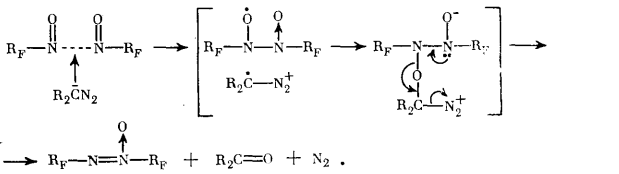
Later, other workers[134] confirmed this hypothesis also by the observation that the interaction of trifluoronitrosomethane with diphenyl- and dimethyl-diazomethanes results in the formation of a dialkyl ketone:



The following mechanism of the reaction between trifluoronitrosomethane and bis(trifluoromethyl)diazomethane has been suggested:



The authors believe that, when other diazoalkanes [Ph_2CN_2, $(CH_3)_2CN_2$] are used in this reaction, a nitrone is not formed and suggest a mechanism with charge transfer (at low temperatures in the condensed phase):



Mixed fluoroazoxyalkanes were obtained in the same study[134]:

$$CF_3{-}NO + C_3H_7{-}NO + R_2CN_2 \rightarrow CF_3{-}\underset{\downarrow}{N}{=}N{-}C_3F_7 + CF_3{-}\underset{\downarrow}{N}{=}N{-}C_3F_7 \ .$$
$$O \qquad\qquad O$$

On reaction with diphenyldiazomethane, perfluoronitroso-t-butane gives rise to oxaziridine[135], while other fluoronitroso-alkanes react with diazoalkanes to form copolymers[136,137]:

$$(CF_3)_3C{-}N{=}O + Ph_2CN_2 \rightarrow (CF_3)_3C{-}\underset{\diagdown\ \diagup}{N}\!\!-\!\!O + N_2 \ ;$$
$$CPh_2$$
$$R_F{-}NO + X{-}CHN_2 \rightarrow (-\underset{R_F}{\underset{|}{N}}{-}O{-}\underset{X}{\underset{|}{CH}}{-})_n + N_2 \ ;$$
$$R_F{=}CF_3,\ C_3F_7;\ X{=}H,\ CF_3 \ .$$

Methylisonitrile deoxygenates trifluoronitrosomethane with formation of a carbodi-imide[138]:

$$CF_3{-}NO + \ddot{C}{=}N{-}CH_3 \xrightarrow[-O{=}C{=}N{-}CH_3]{} [CF_3{-}\ddot{N}] \xrightarrow{\ddot{C}{=}N{-}CH_3} CF_3{-}N{=}C{=}N{-}CH_3 \ .$$

(e) Substitution of the Nitroso-Group

Substitution of the nitroso-group by a halogen. The low energy of the C–N bond in fluoronitroso-compounds promotes easy substitution of the nitroso-group. This was first observed[115] in the thermal decomposition of 1,2-dichlorotrifluoronitrosoethane (see above). The nitroso-group is readily substituted on interaction of secondary and tertiary fluoronitrosoalkanes with halogens[76,140]:

$$\begin{matrix} CF_3 \\ FSO_2 \end{matrix}\!\!>\!CF{-}NO \xrightarrow{Br_2} \begin{matrix} CF_3 \\ FSO_2 \end{matrix}\!\!>\!CF{-}Br + BrNO \ ;$$
$$(CF_3)_3C{-}NO \xrightarrow{X_2} (CF_3)_3C{-}X + X{-}NO \ ;$$
$$X{=}Cl,\ Br,\ I \ .$$

It is of interest that the substitution of the nitroso-group in 2-chloro-trifluoro-1-nitro-2-nitrosoethane[140] occurs only on treatment with chlorine, while treatment with bromine and iodine results in the formation of a dichloro-compound, which is a disproportionation product of the initial nitrosoalkane:

$$O_2N{-}CF_2{-}CFCl{-}NO \xrightarrow{Cl_2} O_2N{-}CF_2{-}CFCl_2 + Cl{-}NO \ .$$

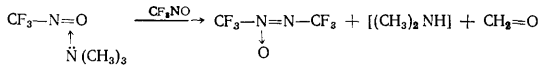
The formal substitution of the nitroso-group by a hydrogen atom takes place on hydrolysis and alcoholysis of alkyl hexafluoro-2-nitrosobutyrates[74,141] and (hexafluoroisopropyl-2-nitroso)diethyl phosphate[68] and on interaction of perfluoronitroso-t-butane with *N,N*-dimethylaniline, aniline, or ethanol[140]:

$$\begin{matrix} X \\ CF_3 \end{matrix}\!\!>\!\underset{\underset{N=O}{|}}{C}{-}C(O)OR \xrightarrow{H_2O(C_2H_5OH)} \begin{matrix} X \\ CF_3 \end{matrix}\!\!>\!\underset{\underset{H}{|}}{C}{-}C(O)OR \ ;$$
$$X{=}CF_3;\ C(O)OR$$
$$(C_2H_5O)_2P{-}O{-}\underset{\underset{N=O}{|}}{C}(CF_3)_2 \xrightarrow{H_2O(C_2H_5OH)} (C_2H_5O)_2P{-}O{-}\underset{\underset{H}{|}}{C}(CF_3)_2 \ ;$$
$$(CF_3)_3C{-}N{=}O{-}\begin{cases} H{-}\langle\!\rangle{-}NX_2 \rightarrow O{=}N{-}\langle\!\rangle{-}NX_2 \\ H{-}OC_2H_5 \rightarrow O{=}N{-}OC_2H_5 \end{cases} + (CF_3)_3C{-}H \ ;$$
$$X{=}H;\ CH_3.$$

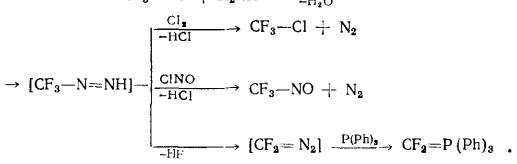
Interaction with tetrafluorohydrazine. On interaction with tetrafluorohydrazine, the nitroso-group is substituted only in tertiary fluoronitroso-compounds[142–144], in which the dissociation energy of the C–N bond is lowest:

$$\begin{matrix} CF_3 \\ CF_3{-}C{-}NO \\ R \end{matrix} \xrightarrow{N_2F_4} \begin{matrix} CF_3 \\ CF_3{-}C{-}NF_2 \\ R \end{matrix} + \begin{matrix} CF_3 \\ CF_3{-}C{-}N{=}NF \\ R \end{matrix}\!\!\!

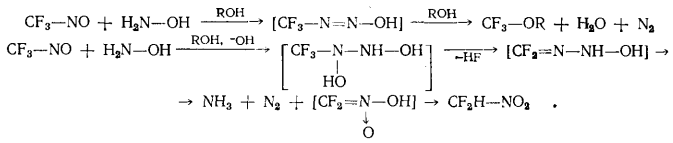
results in the formation of hexafluoroazoxymethane:



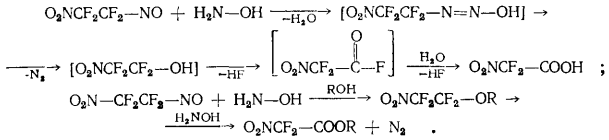
The reaction of trifluoronitrosomethane with ammonia[150] leads to an unstable azo-compound, whose formation has been demonstrated by chemical transformations:



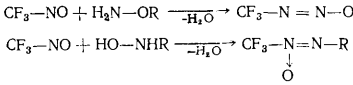
The interaction of trifluoronitrosomethane with hydroxylamine in an alcoholic medium leads to the formation of alkyl trifluoromethyl ether, while the product in an alcoholic alkaline medium is difluoronitromethane[150]:



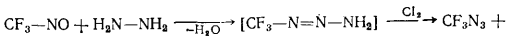
Tetrafluoro-1-nitro-2-nitrosoethane is decomposed by hydroxylamine to difluoronitroacetic acid[153], while in an alcoholic medium the alkyl ester of the acid is formed:



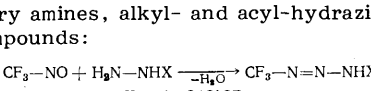
The reactions of trifluoronitrosomethane with *O*-alkylhydroxylamines[150] result in the formation of azo-compounds, while the reactions with *N*-alkylhydroxylamines[154] yield azoxy-compounds:



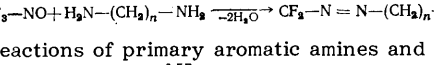
Hydrazine reacts with trifluoronitrosomethane[150,155] to form an unstable azo-compound, which decomposes under the influence of chlorine to trifluoromethyl azide:



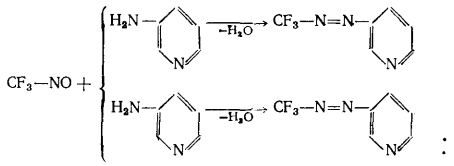
Like primary amines, alkyl- and acyl-hydrazines form aminoazo-compounds:



Trifluoronitrosomethane reacts with diamines[156] to form bisazo-compounds;



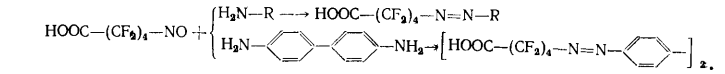
The reactions of primary aromatic amines and diamines with trifluoronitrosomethane[157] also yield azo- and bisazo-compounds respectively. 2-Aminopyridine and 3-aminopyridine[158] react with trifluoronitrosomethane to give azo-derivatives, while 4-aminopyridine does not react with trifluoronitrosomethane:



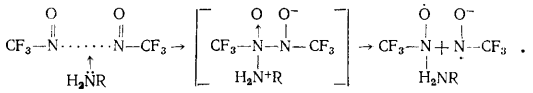
Electron-accepting groups in the α-position with respect to the amino-group [$(H_2N)_2C{=}O$, H_2NCOOH] lower the nucleophilicity of such amines and prevent their reaction with trifluoronitrosomethane[159].

Electron-accepting groups in the β-position with respect to the amino-group ($H_2N{-}CR^1R^2{-}COOR$) do not prevent the formation of the azo-compound[160,161]. *p*-Aminobenzoic acid also enters into this reaction[162].

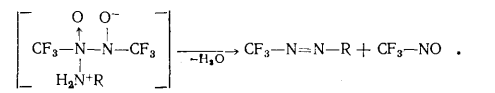
Carboxylic α,ω-fluoronitrosoacids[163] react with amines and diamines to form azo- and bisazo-compounds respectively:



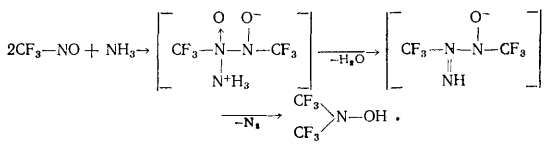
Radical-ions, formed via a charge-transfer complex, have been detected by EPR in the interaction of trifluoronitrosomethane with amines at low temperatures[164,165]:



On this basis, the following mechanism of the interaction of amines with trifluoronitrosomethane has been proposed[165]:

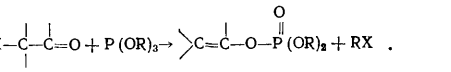


The suggested mechanism for the reaction of trifluoronitrosomethane with ammonia is



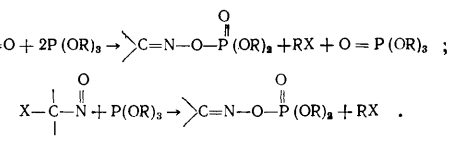
(b) Interaction with Phosphorous Acid Esters and Phospholans

The analogy between the nitroso-group and the carbonyl group is manifested strikingly also in the reactions of nitrosoalkanes with phosphorus acid esters. The Perkow reaction between α-halogenocarbonyl compounds and trialkyl phosphites is widely known[166–168]:

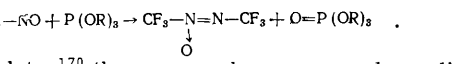


Allen[169] showed that geminal halogenonitro- and halogenonitroso-alkanes react analogously, forming the phosphates of

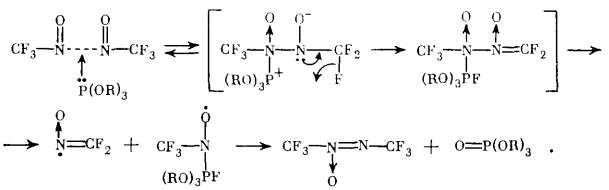
the corresponding oximes:



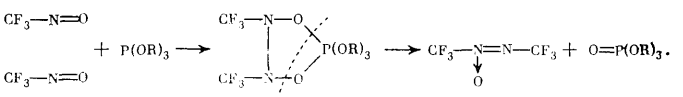
The first fluoronitroso-compound investigated in the reaction with phosphites was trifluoronitrosomethane[86]:



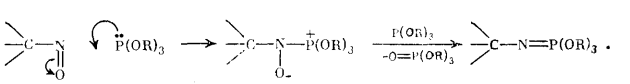
Several years later[170] the same workers proposed a radical-ion mechanism for this reaction on the basis of an EPR study:



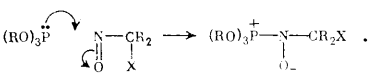
By analogy with hexafluoroacetone[171], the possibility of another version has been suggested[144]:



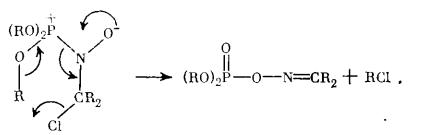
A number of general features have been established in studies of the interaction of fluoronitroso-compounds with phosphite esters[172-174]. The first step in the reaction is attack by the phosphorus atom on the nitrogen atom. Neutral phosphites react with tertiary fluoronitrosoalkanes to form phosphazo-compounds:



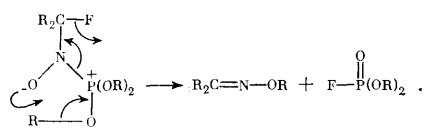
The interaction of fluoro-α-halogenonitrosoalkanes involves the intermediate formation of the *O*-anion of a hydroxylamine, whose subsequent fate depends on the nature of the halogen X:



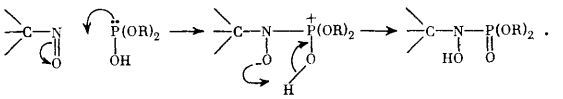
When X = Cl, the alkyl chloride is split off with formation of the products of the Allen reaction:



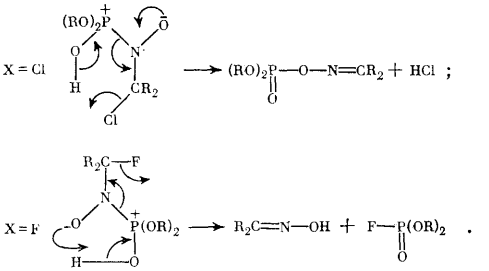
When X = F, the fluoro-oxime group acquires "pseudo-halogen" properties as a result of the high strength of the P–F bond and is split off with the alkyl group:



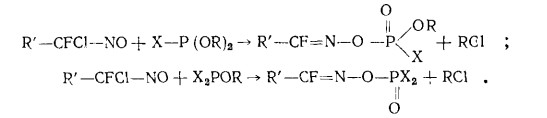
Trifluoronitrosomethane and perfluoronitroso-t-butane react with acid phosphites to form phosphorylated hydroxylamines (similarly to compounds with a carbonyl group[175,176]):



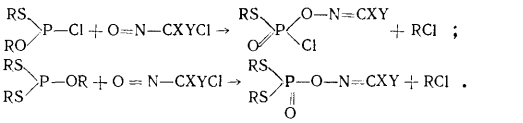
The interaction of fluoro-α-halogenonitrosoalkanes with acid phosphites results in the formation of the *O*-anion of a hydroxylamine, which splits off hydrogen chloride in the presence of a chlorine in the α-position and an oxime in the presence of a fluorine atom:



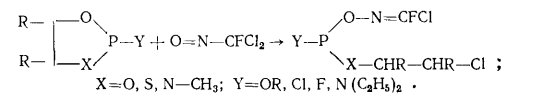
Similar reactions have been achieved with various α-chloronitrosoalkanes and halogenoalkyl phosphites[177]. In this case the products of the Allen reaction are also formed:



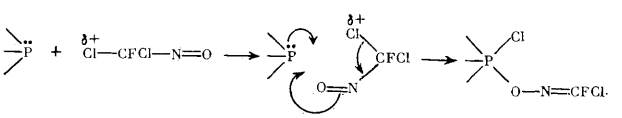
It has likewise been established that, when the alkyl halide is split off in the Allen reaction, the alkyl group is abstracted only from the alkoxy-group and not the thioalkoxy-group:



In subsequent studies[178-181] it was shown that phospholans containing at least one oxygen atom at the phosphorus atom can also enter into the Allen reaction with α-chlorofluoronitroso-compounds:

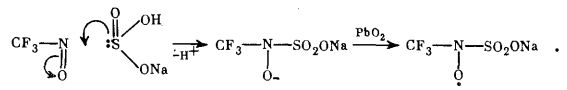


Having surveyed the available experimental data, Maleikin et al.[182] proposed a mechanism for the Allen reaction which we believe to be unlikely; it involves initial attack by the unshared electron pair of the phosphorus atom on the positively polarised chlorine atom (cf. Dyatkin et al.[174]):

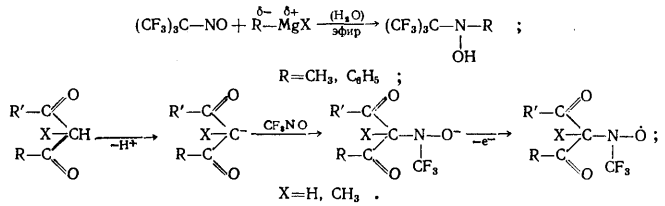


(c) Interaction with Other Nucleophiles

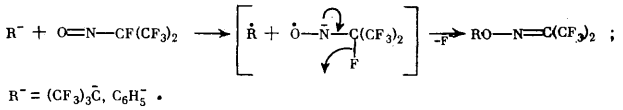
Like carbonyl compounds[183], trifluoronitrosomethane combines with sodium bisulphite[184]:



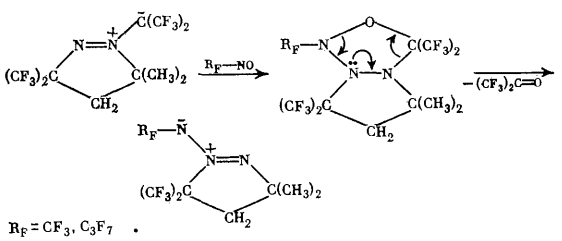
When nitrosoperfluoroalkanes were allowed to react with Grignard reagents[185] and α-diketones[186], the products of the attack by the carbanion on the nitrogen atom of the nitroso-compound were obtained:



It has been reported[187] that carbanions can attack also the oxygen atom in 2-nitrosoperfluoropropane:



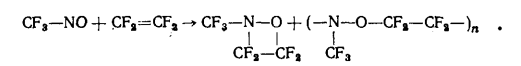
It may be that such interaction also takes places with other carbanions[188]:



8. Reactions with Unsaturated Compounds

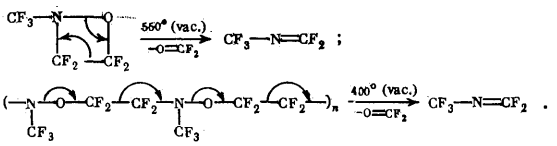
(a) Interaction with Fluoro-olefins

The development of the chemistry of fluoronitroso-compounds is perhaps most closely related to the discovery of the reaction of fluoronitrosoalkanes with fluoro-olefins from whose products copolymers with unique properties were isolated. The interaction of trifluoronitrosomethane with tetrafluoroethylene was first investigated by Barr and Haszeldine[189] in 1955:

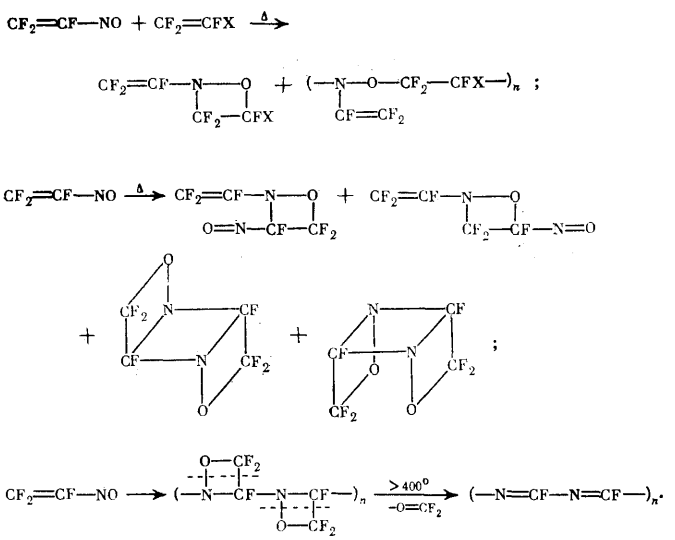


Later it was established that other fluoronitroso-compounds ($O_2NCF_2CF_2NO$,[54,190] C_2F_5NO, and $ClCF_2NO$ [46]) and fluoro-olefins ($CF_2=CFH$,[191-193] $CF_2=CFCL$,[193] $CF_2=CF-CFCl-CF_2CL$,[194] and $CF_2=CF-COF$ [195]) react analogously.

The ability of the copolymers and the oxazetidines formed simultaneously to produce on pyrolysis fluoroazomethines (in particular perfluoro-2-azapropane), with unusual chemical properties and high reactivity, whose chemistry is still being investigated, constitutes a very important property:



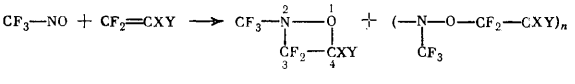
Trifluoronitrosoethylene has very interesting properties, which are a combination of those of a nitrosoalkane and a fluoro-olefin[10,196,197]. This fluoronitrosoalkene reacts with both fluoro-olefins and with itself, forming oxazetidines, polymers, and bicyclic compounds:



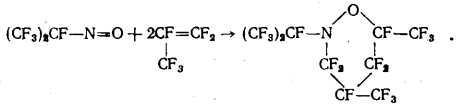
The interactions of fluoronitrosoalkanes with fluoro-olefins have a number of characteristic features.

1. At room temperature and below, a copolymer is formed preferentially, while on raising the temperature to 100 °C, the main product becomes an oxazetidine[46,54,58,189,191,194,196].

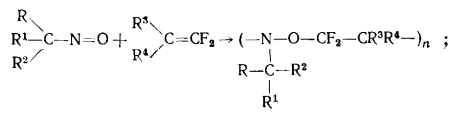
2. The interaction of fluoronitroso-compounds with asymmetric fluoro-olefins involves different modes of addition[111]. When an oxazetidine is formed, the difluoromethylene group of the olefin adds to the nitrogen atom, while on formation of a copolymer it adds to the oxygen atom:



3. Steric factors exert a significant influence on the formation of the oxazetidine[41,111]. The branching of the alkyl group of the fluoronitrosoalkane hinders the formation of the oxazetidine to a lesser extent than the branching in the fluoro-olefin. If only one of the reactants in the interaction of a fluoronitrosoalkane with a fluoro-olefin is branched in the fluorocarbon chain, an oxazetidine with a substituent predominantly in the 4-position is formed[41,65,111]. If both reactants are branched, an oxazetidine is not formed. Only in one instance has it been possible to obtain a cyclic product in the reaction of a branched fluoronitrosoalkane with a substituted fluoroethylene[198]:



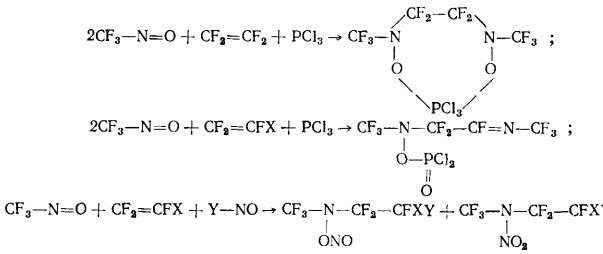
It is of interest that non-fluorinated nitroso-t-alkanes give rise to copolymers with both unsubstituted and substituted fluoro-olefins[199,200]:



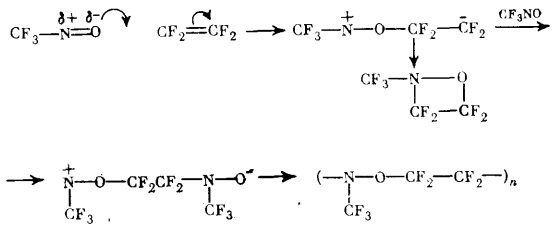
R, R^1, R^2 = alkyl, aryl, cycloalkyl; R^3, R^4 = F, Cl, H .

The introduction of hydrogen atoms into the tetrafluoroethylene molecule diminishes the reactivity with respect to trifluoronitrosomethane and prevents the formation of an oxazetidine[192].

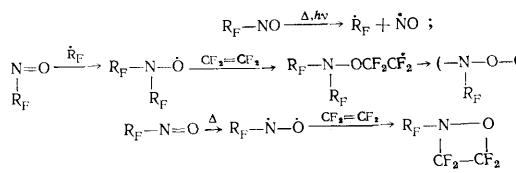
When trifluoronitrosomethane reacts with tetrafluoroethylene in the presence of phosphorus trichloride, cyclic and linear derivatives of phosphoric acid are formed, while in the presence of nitrosyl chloride or nitrogen trioxide the products are *N*-nitrites and *N*-nitro-compounds[22,201-203]:



A unanimous view on the mechanism of the reactions of fluoronitrosoalkanes with fluoro-olefins has not yet been established. An ionic mechanism was proposed initially[189]

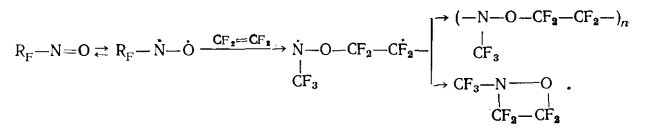


Later the same workers replaced it by a radical mechanism[7]:

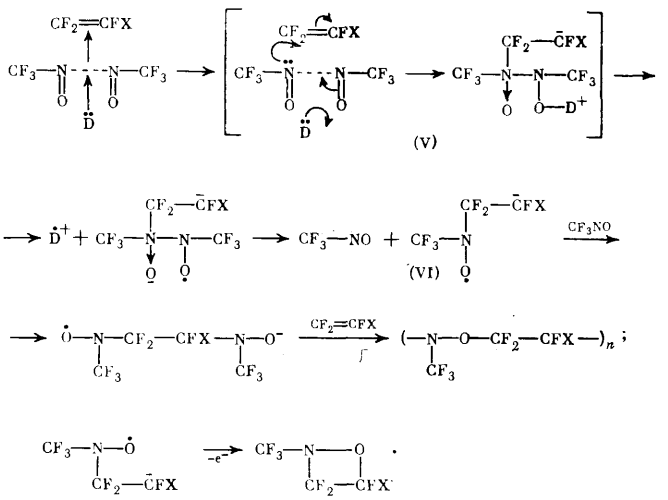


The following facts have been adduced in favour of the radical mechanism. Irradiation of the reaction mass with ultraviolet light or addition of t-butyl peroxide doubles the polymer : oxazetidine ratio. The addition of hydroquinone lowers by a factor of 2 the rate of reaction and diminishes by a factor of 8 the polymer: oxazetidine ratio.

Crawford and co-workers[193-204] also reject the ionic mechanism on the grounds that the copolymerisation takes place in an aqueous medium in the presence of classical deactivators of carbanions such as CO_2, BF_3 etherate, and $TlCl_4$ and that the presence of radical chain-transfer agents diminishes the molecular weight of the copolymer. However, they claim that the radical process is not initiated with homolytic dissociation of the C–N bond but takes place with formation of radicals arising on interaction of the fluoro-olefin with the fluoronitrosoalkane, which passes to the triplet state at the copolymerisation temperature:



The study of mixtures of trifluoronitrosomethane with various fluoro-olefins[205-207] by EPR led to the detection of paramagnetic species, which were assumed to be of the radical-ion type. Having failed to detect biradical species, whose existence had been predicted by Haszeldine and Crawford (see above), Ginsburg et al.[206] rejected the radical mechanism and proposed a radical-ion mechanism according to which a molecule of trifluoronitrosomethane, enriched by an electron donor (the OH^- species present in solution, metal ions, or the nuclophilic solvent), attacks the positively polarised difluoromethylene group of the fluoro-olefin with formation of a radical-ion, which enters into further reactions:



It was established by low-temperature thermography[207] that the formation of associated species (V) on reaction with the electron-donating medium occurs at temperatures between -130 ° and -80 °C with evolution of heat. The radical-ions (VI) are produced at higher temperatures. An electron-donating medium promotes the appearance of paramagnetic species at lower temperatures than in perfluorinated solvents or in the absence of solvents.

The size of the substituent in the fluoro-olefin does not influence significantly the ease of the above reactions. Nor is there a clear-cut correlation between the inductive influence of the substituent and the temperature at which the radical-ion is formed[207].

A detailed study of the kinetics of the copolymerisation of trifluoronitrosomethane and tetrafluoroethylene[208] again confirmed the hypothesis of the radical mechanism of the copolymerisation reaction. It was shown that the rate of formation of the copolymer obeys the equation

$$\partial [C]/\partial t = K_1 [CF_3{-}NO]^{3/2} [CF_2 = CF_2] \ .$$

This equation is also valid for the gas phase and for a homogeneous solution in fluorocarbon solvents at temperatures between -36° and -80 °C with different ratios of the initial reactants. On the basis of this equation, the possibility of a 1 : 1 complex of the monomers is rejected, since the rate of

formation of the copolymer would then have been proportional to $[CF_3NO]^{1/2}$, and the following mechanism is proposed:

$$3CF_3{-}NO \rightarrow \dot{R}^1 + \dot{R}^2$$
$$\dot{R}^1 + CF_2{=}CF_2 \rightarrow R^1{-}CF_2\dot{C}F_2,\ \dot{R}^2 + CF_2{=}CF_2 \rightarrow R^2{-}CF_2\dot{C}F_2\ ;$$

for chain initiation,

$$R{-}CF_2\dot{C}F_2 + \underset{\underset{CF_3}{|}}{N}{=}O \rightarrow R{-}CF_2CF_2{-}\underset{\underset{CF_3}{|}}{N}{-}\dot{O} \xrightarrow{CF_2=CF_2} R{-}CF_2CF_2{-}\underset{\underset{CF_3}{|}}{N}{-}O{-}CF_2\dot{C}F_2\ .$$

for chain propagation, and

$$2\,(R^1{-}\underset{\underset{CF_3}{|}}{N}{-}\dot{O}) \rightarrow \text{copolymer}$$

for chain termination. This mechanism requires a steady-state concentration of the radicals proportional to $[CF_3NO]^{3/2}$, which agrees with experiment. It has been suggested that the chain propagation proceeds via the interaction of $R^1{-}\underset{\underset{CF_3}{|}}{N}{-}\dot{O}$ with tetrafluoroethylene. The presence of this radical has been confirmed rigorously by EPR. The radical $R^1{-}\underset{\underset{CF_3}{|}}{N}{-}O{-}CF_2{-}\dot{C}F_2$ evidently reacts very rapidly with trifluoronitrosomethane, since it has not been detected in the EPR spectra even in a mixture of trifluoronitrosomethane with an excess of tetrafluoroethylene. The radical-ions mentioned above[207] were not detected in the above study and chain propagation via an ionic mechanism is thought to be unlikely.

In the proposed mechanism[208] the structures of the radicals $\dot{R}^1$ and $\dot{R}^2$ were not established but their concentration is proportional to $[CF_3NO]^{3/2}$, which clearly confirms the three-step initiation mechanism. The rate of formation of these radicals depends greatly on the nature of the solvent, which does not agree with earlier ideas concerning the initiation of the process in the homolysis of the C–N bond in trifluoronitrosomethane. It is also emphasised that the usual radical process initiators do not accelerate the copolymerisation in this instance. However, it has been established that the bis(trifluoromethyl)nitroxy-radical initiates specifically the copolymerisation of trifluoronitrosomethane and tetrafluoroethylene.

Kinetic studies[208,209] of the formation of oxazetidine showed that the rate of its formation obeys the equation

$$\partial[O]/\partial t = K_2[CF_3NO][CF_2{=}CF_2]\ .$$

The authors concluded that this is not a radical-chain process, since the kinetic data are consistent with a four-centre transition state but do not enable one to distinguish between a concerted mechanism and an ionic transition state.

A version of radical initiation was proposed[210] on the basis of the electronic spectra of copolymers of trifluoronitrosomethane and fluoro-olefins and the results of calculations by the INDO SCFMO method. It involves thermal excitation of the trifluoronitrosomethane molecule to the triplet state with subsequent addition of a fluoro-olefin molecule to the nitrogen or oxygen atom:

$$CF_3{-}N{=}O \xrightarrow{\Delta} CF_2{-}\dot{N}{-}\dot{O}\ ;$$

$$CF_3{-}\dot{N}{-}\dot{O} + CF_2{=}CF_2 \begin{cases} \rightarrow \dot{N}{-}O{-}CF_2{-}\dot{C}F_3 \quad (A) \\ \qquad\quad | \\ \qquad\quad CF_3 \\ \rightarrow \dot{O}{-}\underset{\underset{CF_3}{|}}{N}{-}CF_2{-}\dot{C}F_2 \quad (B) \end{cases};$$

$$CF_3{-}N{=}O + \begin{cases} \dot{N}{-}O{-}CF_2{-}\dot{C}F_2 \xrightarrow{CF_2=NO} \dot{N}{-}O{-}CF_2CF_2O{-}\underset{\underset{CF_3}{|}}{N} \quad (C) \\ \quad | \\ \quad CF_3 \quad (A) \\ \qquad\qquad \rightarrow \dot{N}{-}O{-}CF_2CF_2{-}\underset{\underset{CF_3}{|}}{N}{-}O \quad (D) \\ \dot{O}{-}\underset{\underset{CF_3}{|}}{N}{-}CF_2{-}\dot{C}F_2 \xrightarrow{CF_2=NO} \dot{O}{-}\underset{\underset{CF_3}{|}}{N}{-}CF_2CF_2{-}\underset{\underset{CF_3}{|}}{N}{-}\dot{O} \quad (E)\ . \\ \quad | \\ \quad CF_3 \quad (B) \end{cases}$$

The excitation energy of the trifluoronitrosomethane was estimated as 28 kcal mol^{-1}, which is sufficient for the operation of the proposed mechanism. A regularity was observed in the spectra of the copolymers $(-\underset{\underset{CF_3}{|}}{N}{-}O{-}CF_2{-}CFX)_n$, indicating that, apart from the radical D (which is the main one), there is a possibility of the formation also of other radicals (C and E).

Simultaneously with the studies of Crabtree and co-workers[208,209] and Clark et al.[210], a report was published in 1972 [211] concerning the interaction of trifluoronitrosomethane with fluoro-olefins in a condensed phase in the presence of halogens and sulphur dichloride as copolymerisation initiators:

$$CF_3{-}NO + CF_2{=}CFR \xrightarrow{XX'} X{-}CF_2{-}CFR{-}(-\underset{\underset{CF_3}{|}}{N}{-}O{-}CF_2{-}CFR-)_n{-}X'\ ;$$
$$XX' = Cl_2,\ Br_2,\ I_2,\ SCl_2\ .$$

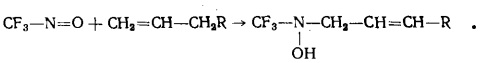
A radical mechanism has been proposed for this reaction. On the basis of the analysis of the EPR spectra, it is claimed that the reaction is initiated by the trifluoromethyl radical arising from a charge-transfer complex in which the halogen molecule functions as the donor.

However, the authors[211] claim that this is a special case and that in general the copolymerisation of trifluoronitrosomethane with fluoro-olefins takes place via an ionic and not a radical mechanism and the latter is possible only under special conditions (for example, in the presence of halogens). Thus the problem of the mechanism of the interaction of fluoronitrosoalkanes with fluoro-olefins has still not been ultimately resolved at the present time but one should note that the evidence for radical copolymerisation is fairly convincing.

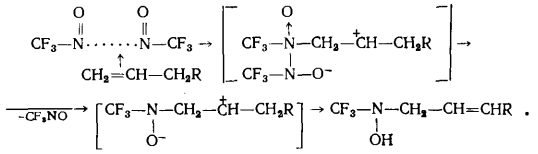
(b) Interaction with Perfluoro-olefins

Between 1962 and 1974, experimental data were accumulated on the interaction of trifluoronitrosomethane with various alkenes[138,205,212–214]. It was found that non-fluorinated olefins have only partially the same properties as their fluorinated analogues in relation to fluoronitrosoalkanes. Among all the alkenes investigated, only styrene[138], vinyl acetate[205], and methyl acrylate[214] react with trifluoronitrosomethane to form oxazetidines, while only ethylene[192] forms a copolymer by reaction with trifluoronitrosomethane with a yield of 75% in 22 months at 20 °C.

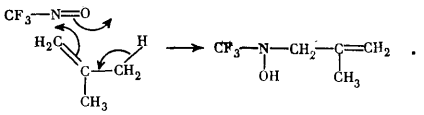
All other olefins form alkenyltrifluoromethylhydroxylamines on reaction with trifluoronitrosomethane:



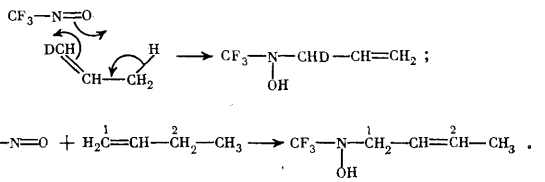
A mechanism postulating the intermediate formation of donor–acceptor charge-transfer complexes was proposed for these reactions[215]:



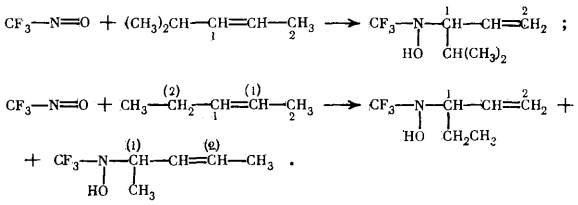
Haszeldine and co-workers[212] proposed a mechanism for the interaction of trifluoronitrosomethane with isobutene involving nucleophilic attack by a carbon atom in the unsaturated bond on the nitrogen atom of the fluoronitrosoalkane:



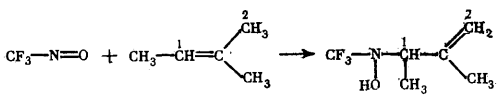
Subsequently they developed this mechanism in greater detail. It was shown in relation to 20 alkenes that in these reactions the C(1) carbon atom attacks the nitrogen atom of trifluoronitrosomethane and that hydrogen is transferred from C(2) to the oxygen atom[216]†:



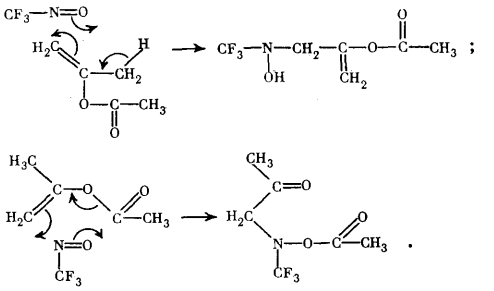
Allyl hydrogen is transferred from the least substituted carbon atom:



The least substituted carbon atom in the unsaturated bond attacks the nitrogen atom:

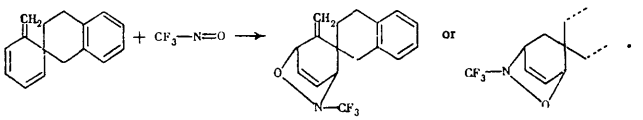


Attack on the nitrogen atom of trifluoronitrosomethane by the methylene group of isopropenyl acetate leads to the formation of two products:



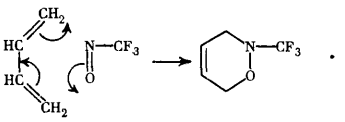
(c) Interaction with Dienes

Trifluoronitrosomethane is one of the most reactive dienophiles in Diels–Alder reactions[217]. This was first observed when the [2 + 4] cyclic adduct of trifluoronitrosomethane with spiro-di-*o*-xylylene was obtained[218]:

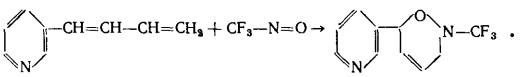


Later it was shown[219] that a copolymer is also formed under these conditions.

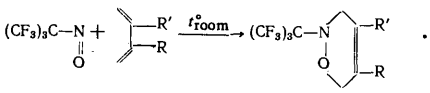
Trifluoronitrosomethane readily reacts with butadiene at −78 °C and an oxazine is formed in 97% yield:



A similar reaction takes place also with β-butadienylpyridine[220]:



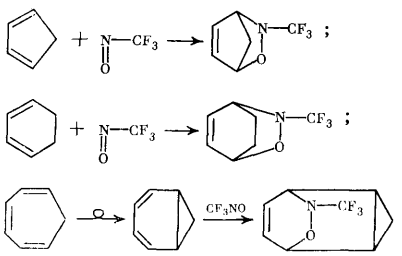
On the other hand, nitroso-t-butane does not react with dienes at all, while its perfluoro-analogue forms oxazines on reaction with butadiene and its derivatives[185] at room temperature:



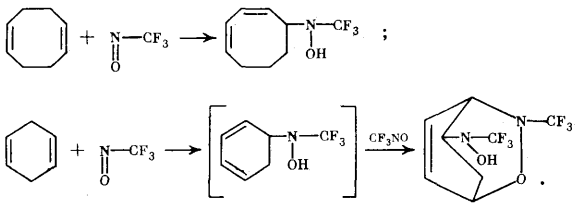
Apart from the oxazine, a copolymer is also formed in this reaction[221]. The ratio of the cyclic product to the copolymer increases as the reaction temperature is reduced, while in the interaction of fluoronitroso-compounds with fluoro-olefins the opposite behaviour is observed (see above).

† The numeral 1 designates the carbon atom attacking the nitrogen atom. The numeral 2 designates the carbon atom from which the hydrogen atom migrates.

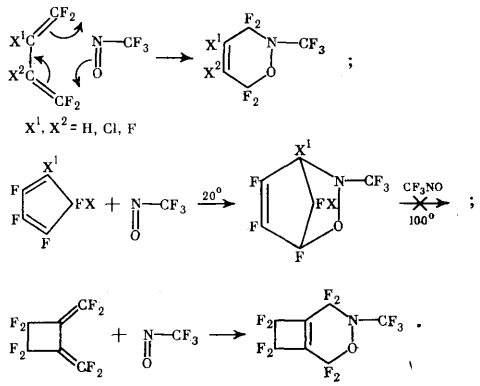
Cyclic conjugated dienes also enter into the Diels–Alder reaction with trifluoronitrosomethane[216,222]:



Non-conjugated cyclic dienes form hydroxylamines on reaction with trifluoronitrosomethane[216] as a result of the attack of the carbon atoms of the double bond on the nitrogen atom and the migration of the allyl hydrogen atom to the oxygen atom:



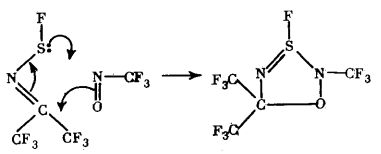
Trifluoronitrosomethane is capable of functioning as the dienophile also in relation to conjugated fluorine-containing aliphatic[194,223,224] and cyclic dienes[225–288]:



Hexafluorobutadiene reacts with various fluoronitroso-compounds more slowly than butadiene[221]. The reaction with trifluoronitrosomethane is slower by a factor of 40 and that with tetrafluoro-1-nitro-2-nitrosoethane by a factor of 600.

A radical-ion mechanism of the interaction of trifluoronitrosomethane with polyfluorinated and non-fluorinated dienes has been put forward on the basis of EPR spectra[222] (analogously to the mechanism described above).

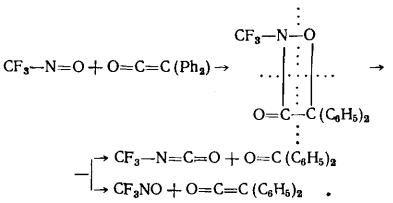
An unusual [2 + 3] cycloaddition takes place on interaction of trifluoronitrosomethane with hexafluoroacetone fluorosulphenylimine[229]:



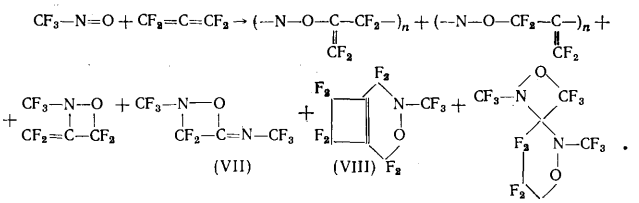
(d) Interaction with Cumulenes

The interaction of fluoronitroso-compounds with cumulenes has been investigated only in relation to trifluoronitrosomethane. Like other unsaturated compounds, cumulenes are capable of forming oxazetidines and polymers on reaction with trifluoronitrosomethane.

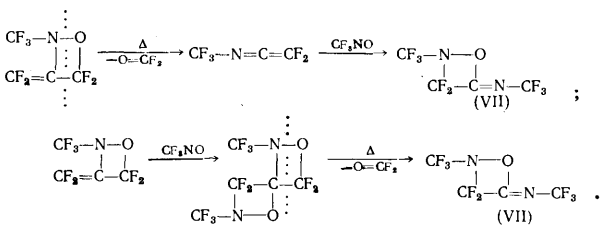
Diphenyl ketone reacts with trifluoronitrosomethane to form an oxazetidine, which can be pyrolysed via two pathways[138]:



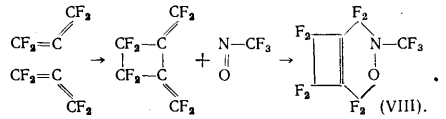
Tetrafluoroallene reacts with trifluoronitrosomethane to form a complex mixture of substances[230], from which polymers, oxazetidines, oxazines, and spiro-compounds were isolated:



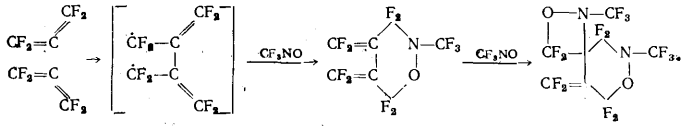
The formation of compound (VII) is explained by the following mechanisms:



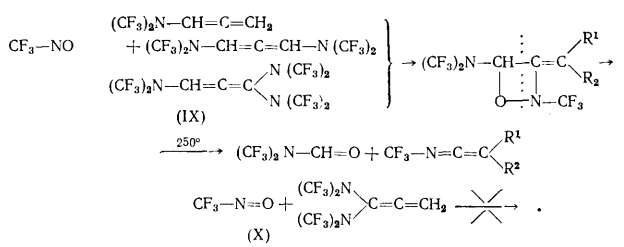
Compound (VIII) is formed from the tetrafluoroallene dimer as described by Banks et al.[228]:



The following mechanism has been postulated to account for the formation of spiro-compounds:

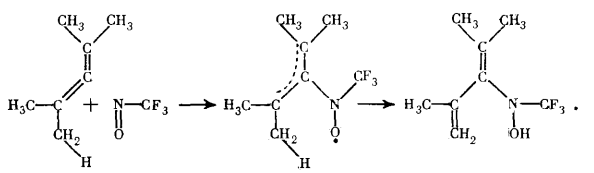


N,N-Bis(trifluoromethyl)aminoallenes react with trifluoronitrosomethane to form only oxazetidines[231,232] whose pyrolysis yields bis(trifluoromethyl)formamide and cumulated



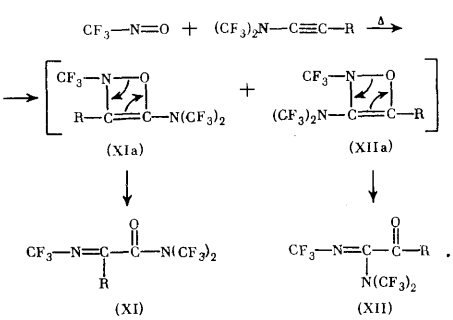
For reasons which are obscure[232], compound (X) does not enter into this reaction, while its close structural analogue (IX) reacts with trifluoronitrosomethane to form an oxazetidine.

Tetramethylallene forms the corresponding hydroxylamine on interaction with trifluoronitrosomethane[233]. The authors suggest the possibility of a mechanism involving a biradical:



(e) Interaction with Acetylenes

The reaction of fluoronitroso-compounds with acetylenes has been studied in only one instance[234]. The formation of the products of the reaction of trifluoronitrosomethane with bis(trifluoromethyl)aminoacetylenes has been explained by the intermediate formation of oxazetidines:



When R = H, Br, or CF_3, the main product is compound (XI), evidently as a consequence of the preferential formation of the less sterically hindered oxazetidine (IXa), whereas for R = $N(CF_3)_2$ only one reaction product is naturally obtained.

IV. THE PROPERTIES AND APPLICATIONS OF COPOLYMERS OF FLUORONITROSO-COMPOUNDS

Data on the copolymers of fluoronitrosoalkanes with fluoro-olefins first appeared in 1955.[189,235] The copolymers immediately attracted much attention having shown a series of interesting and useful properties—resistance to concentrated sulphuric acid, 50% potassium hydroxide solution, and hot aqueous alkali[189], thermal stability in air up to 200 °C, and retention of elasticity at −30 °C.[236]

Further studies yielded a large number of copolymers of fluoronitrosoalkanes with various unsaturated compounds. Whereas the number of studies on the chemical properties of fluoronitrosoalkanes has decreased appreciably in recent years, in the field of copolymers of fluoronitro-compounds publications have continued to appear up to the present time in which further new properties and applications of these substances are described.

Several reviews have been devoted in recent years to the synthesis and properties of the copolymers of fluoronitroso-alkanes[237–242].

All the copolymers of fluoronitrosoalkanes can be divided by convention into three large groups.

1. The copolymers of fluoronitrosomethane and tetrafluoro-ethylene.
2. The copolymers of other fluoronitrosoalkanes and various fluoro-olefins.
3. Ternary copolymers.

1. The Copolymers of Trifluoronitrosomethane and Tetra-fluoroethylene

It was noted above that the preferential formation of the copolymer relative to the oxazetidine in the interaction of trifluoronitrosomethane with tetrafluoroethylene takes place at 0 °C and below. Depending on the copolymerisation conditions, a liquid[189,235] or solid[236,243] copolymer can be obtained. Usually efforts are made to obtain rubber-like copolymers with a molecular weight in excess of 10^6.

The copolymers of trifluoronitrosomethane with tetrafluoro-ethylene $(-N(CF_3)-O-CF_2-CF_2-)_n$ are highly resistant to chemical reagents and ozone-induced and natural ageing, are frost resistant (the glass point of the copolymer with a molecular weight in excess of 10^6 is −51 °C), and their properties remain unchanged for a long time at 200 °C. The vulcanisates are resistant to aromatic and aliphatic hydrocarbons, alcohols, ethers, aldehydes, ketones, and concentrated acids, do not ignite, and when placed in a flame evolve pyrolysis products which quench the flame[244,245]. Such copolymers do not ignite even in pure oxygen[241]. They are soluble only in halogenoalkanes, cyclic perfluoro-ethers, and perfluorotri-butylamine. In the presence of strong bases, for example, triethylamine, the copolymer readily decomposes[242]. Difluoro-phosgene and perfluoro-2-azapropene are formed on radiolysis and thermal and photochemical decomposition of the copolymer[246].

The inadequate thermal and radiation stability limit the applications of these copolymers. The usual vulcanising agents, employed for hydrocarbon elastomers[241], are unsuitable for them. However, it has been observed that triethylenetetramine and hexamethylenediamine form a network structure in cured rubbers based on raw nitroso-rubbers[247,248].

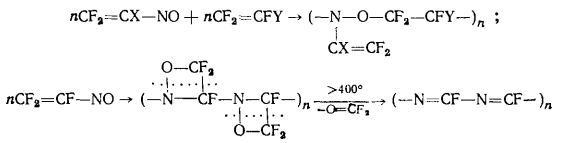
Fillers are used to improve the strength of the copolymers. The most effective is finely ground silica (in the case of amine vulcanisation)[241].

Vulcanisation and addition of various fillers[244,247,249–252] resulted in elastic and thermoplastic copolymers virtually without residual deformation, which are useful as protective coatings and articles[249,253], lubricants[254], and protective low-temperature coatings resistant to highly corrosive oxidants, for example, ClF_3.[250,251]

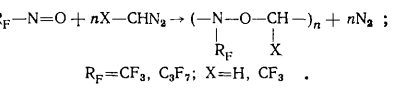
2. The Copolymers of Other Fluoronitrosoalkanes and Different Fluoro-olefins

Thermostable[255,256] and elastic[257] copolymers, which can be used as lubricants and protective coatings for metals[258], have been obtained by the copolymerisation of various perfluoronitrosoalkanes with fluoroethylenes.

Among fluorovinyl nitroso-compounds[259,260], elastic and thermostable polymers have been synthesised by copolymerisation and homopolymerisation:



Copolymers with satisfactory thermal and corrosion stabilities, which can be used as films, protective coatings, gaskets, and washers, have been synthesised from trifluoronitrosomethane and diazoalkanes[136,137]:



The study of the thermal stabilities of raw fluoronitrosorubbers *in vacuo* and in oxygen[261] established that the perfluoro-copolymers are more stable in oxygen.

The vulcanisation of certain raw fluoronitroso-rubbers improves their resistance to solvents and halogen-containing oxidants[262].

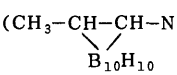
The introduction of various functional groups into the copolymer chain also promotes the appearance of useful properties in the copolymers and improves their capacity for vulcanisation. Both olefins with functions groups [CH_2–C(–CH_3)–$COOCH_3$, CH_2=CH–CN, and CH_2=CH–C_6H_5;[263] CF_2=CF–SO_2F;[264] CF_2=C=CXY;[265,266] CH_2=CH–CH=CH_2;[267] CF_2=CF$(CF_2)_n$–COONa;[268] CF_2=CF–OR [269]] and fluoronitrosoalkanes [O=N–CF_2–COF;[270] O=N–CF_2–$COOCH_3$;[271] O=N–$(CF_2)_n$–COOH [272]] are used in the copolymerisation reaction.

Such copolymers have satifactory thermal and chemical stabilities and can be used as lubricants, waxes, and elastomers[265–268]. Copolymers with improved resistance to oxidants have been obtained[270,271]. Some of them can be used as cation-exchange membranes in the electrolysis of alkali metal halides[272].

3. Ternary Copolymers

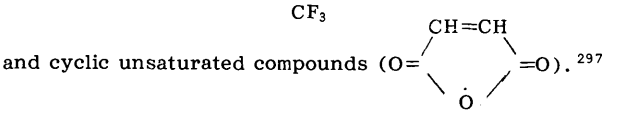
Yet another effective and widely used method for the introduction of functional groups into the polymer chain of raw nitroso-rubbers involves the use in the copolymerisation, apart from the fluoronitrosoalkane and the fluoro-olefin, of a third monomer having an alkenyl or nitroso-group at one end of the molecule and the required functional group at the other. Such copolymers are referred to as ternary polymers or terpolymers.

The most common "third" monomers are nitroso-compounds with functional groups, which consist of carboxylic perfluoronitrosoacids [O=N–$(CF_2)_n$–COOH],[273–282] methyl esters of carboxylic fluoronitrosoacids [O=N–$(CFX)_n$–$COOCH_3$],[283,284] aromatic fluoronitroso-compounds[285–288], aromatic non-fluorinated nitroso-compounds[289], nitrosoethers (O=N–CF_2–CFCl–O–C_2H_5),[290] and 1-methyl-2-nitrosocarbaborane

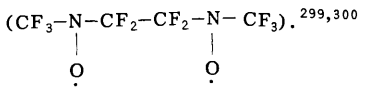


[291]

The following olefins with functional groups have been used: acrylic acid[292,293], unsaturated carboxylic fluoroacids and their esters, metal salts, amides, and nitriles [CF_2=CF–$(CF_2)_n$–A, where A = COOH, COOR, COOM, $CONH_2$, or CN),[294] unsaturated polyether carboxylic fluoroacids and their nitriles, fluorides, esters, metal salts, and dialkylamides [CF_2=CF–O–CF_2–(CFX–O–$CF_2)_m$–$(CFX)_n$–$(CF_2$–O–$CFX)_l$–A, where A = COOH, CN, COF, COOR, COOM, or $CONR_2$],[295] unsaturated fluoroethers with a sulphonyl fluoride group (CF_2=CF–CF_2–CF(–CF_3)–O–CF_2–CF_2–SO_2F),[296]



Such polymers can be vulcanised with metal oxides, metal salts of organic and organofluorine acids (chromium trifluoroacetate), epoxy-compounds[241], poly(butadiene)di-isocyanate [O=C=N–$(CH_2$–CH=CH–$CH_2)_n$–N=C=O] [298] and perfluoro-2,5-diazahexane-2,5-dioxy-biradical



[299,300]

The ternary copolymers of fluoronitrosoalkanes have perhaps the widest range of useful properties among all the copolymers of fluoronitroso-compounds. The unique property of the nitroso-polymers—incombustibility in pure oxygen—has led to their wide-scale employment in the Apollo spaceship[241].

The ternary copolymers have the following properties.

1. Satisfactory chemical and thermal stability[279,287,290,297] and suitability for use as lubricants, washers, and gaskets.
2. High elasticity and tensile strength[273,284–286,288]. Some of them have a relative elongation ranging from 150 to 950% with retention of a high tensile strength[280,281].
3. Thermoplasticity and capacity for being moulded[275,278]. At the same time they are resistant to oxidants such as nitrogen tetroxide[278].
4. The ability to "remember" their initial shape and to recover it on heating[276].
5. A modulus of hardness of 5–200 km cm^{-2} (they are used for the coating of artificial dentures)[301].
6. Elasticity and resistance to the components of rocket fuels (N_2H_4, N_2O_4, ClO_3F, N_2F_4, and ClF_3). They are therefore used in rocket engineering as shutters in the exhaust chambers for the retention of the rocket fuel and oxidant[240,274,277,285,302].
7. Properties permitting their use as binders for rocket fuels and explosives[281,292,293].
8. Properties permitting their employment as cation-exchange membranes in the electrolysis of alkali metal halides[295,296].

However, in planning the applications of such copolymers, one must bear in mind that they evolve toxic gases on decomposition—difluorophosgene, perfluoro-2-azapropene[241], and other fluoroazamethines.

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2-Oxazolidinones

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The synthesis and properties of 2-oxazolidinones and polymers containing 2-oxazolidinone rings are examined. Attention is concentrated on studies devoted to reactions in which the initial monomers are readily available substances produced on a large scale-epoxides and isocyanates. The mechanisms of the formation reactions of oxazolidinones, the catalytic systems employed, and the possible side processes are discussed. The properties and applications of polymers with 2-oxazolidinone rings in the chain are described.
The bibliography includes 218 references.

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I. INTRODUCTION

2-Oxazolidinones occupy a special place among heterocyclic compounds in modern organic chemistry. They are widely used in medicine as drugs and pharmaceutical preparations, as intermediates in the paint and varnish industry, as lubricants, and in many other branches of the national economy. In recent years there has been a considerable development of the synthesis of polymers containing 2-oxazolidinone rings, which are used to prepare adhesives, foams, coatings, fibres, and electrically insulating and other materials, which as a rule have effective physicomechanical properties and high thermal stability and heat resistance.

Numerous methods of synthesis of 2-oxazolidinones have been described in the literature. The most promising method, which is of industrial importance, involves the reaction of epoxides with isocyanates[1]. Numerous studies devoted to this reaction and its employment for the synthesis of a large number of polyoxazolidinones with a wide variety of structures have been published.

There are virtually no Russian and foreign reviews dealing with the present state of the chemistry of 2-oxazolidinones. The present review deals with the available data on the methods of synthesis of 2-oxazolidinones, attention being concentrated on studies of the reactions of epoxides with isocyanates having different structures; the physical and chemical properties of 2-oxazolidinones are discussed. A considerable proportion of the review is devoted to a detailed consideration of the synthesis, reaction mechanisms, properties, and applications of poly-2-oxazolidinones—one of the most important fields of practical application of heterocyclic compounds of this type.

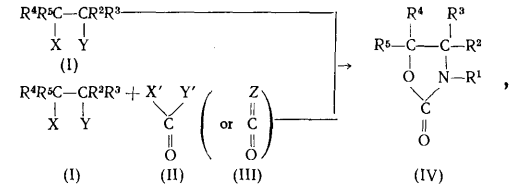
II. THE SYNTHESIS OF 2-OXAZOLIDINONES

The numerous methods of synthesis of 2-oxazolidinones known at the present time can be arranged systematically as follows: (1) cyclisation of β-difunctional compounds in the presence or absence of a cyclising agent; (2) reactions involving the conversion of various (other than epoxides) heterocyclic compounds into 2-oxazolidinones; (3) reactions of epoxides with various compounds.

The reactions are examined below in the same sequence, those of epoxides with isocyanates being dealt with in greater detail, since they are the most promising from the standpoint of practical application.

1. Cyclisation of β-Difunctional Compounds

The reactions involving the synthesis of 2-oxazolidinones from β-difunctional compounds, described in the literature, can be represented schematically in a general form as follows:



where X, Y, X′, and Y′ are functional groups, which are listed in the Table. Hydrogen atoms and aromatic, aliphatic, and alicyclic ligands can be used as substituents R^1, R^2, R^3, R^4, and R^5; R^1 forms part of one of the functional groups of the β-difunctional compound (I).

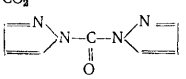
In order to carry out the ring closure reaction, the initial β-difunctional compound (I) is treated with a cyclising agent (II) or (III), which interacts with one of the functional groups of compound (I); this is followed by ring closure with participation of the second functional group. Compound (I) can be cyclised also without adding a cyclising agent, either thermally or under the conditions of acid or base catalysis. The Table presents different versions of the synthesis of 2-oxazolidinones by this method.

The synthesis of 2-oxazolidinone derivatives by the cyclisation of β-hydroxyalkanesulphonic acids (I, X = OH, Y = SO_3H),[40] 1,2-dihalogeno-derivatives (I, X = Y = Hal),[41] β-aminochloroformates (I, X = OCOCl, Y = NH_2),[42] β-hydroxyalkylsemicarbazides [I, X = OH, Y = $N(NH_2)CONH_2$],[43] and nitrenes (I, X = OCO$\ddot{N}$, Y = H) [44] have also been mentioned in the literature.

2. Reactions Involving the Conversion of Various (Other than Epoxides) Heterocyclic Compounds into 2-Oxazolidinones (IV)

Methods of synthesis of 2-oxazolidinones from a series of heterocyclic compounds (mainly three- and five-membered) by their reaction with isocyanates, amines, substituted ureas, carbon dioxide, and other compounds have been described in the literature. In this section we shall consider these reactions with the exception of the conversion of epoxide rings into 2-oxazolidinones.

The synthesis of 2-oxazolidinones (IV) from β-difunctional compounds (I) and cyclising agents (II) or (III).

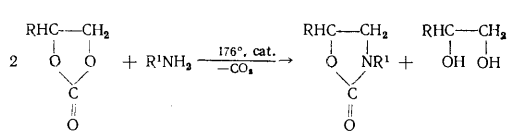
X	Y	Cyclising agent	X′	Y′	Z′	Cyclisation conditions	Refs.
			β-Halogenoamines				
Cl, Br, I	NH_2	Ag_2CO_3	OAg	OAg	—	—	[2]
Cl, Br, I	NH_2	$Na_2CO_3(NaHCO_3)$	ONa	ONa(OH)	—	NaOH	[3]
			β-Halogenoalcohols				
OH	Cl	$COCl_2 + R^1NH_2$	—	—	—	Δ, KOH	[4]
OH	Cl	—	—	—	—	$Na_2NCN + n\text{-}CH_3C_6H_4OCl$	[5]
OH	Cl	$(H_2N)_2CO$	NH_2	NH_2	—	—	[6]
OH	Cl	NCO^-	—	—	—	—	[6]
OH	Br	$R^1NHCOOC_2H_5$	R^1NH	OC_2H_5	—	bases	[7]
OH	Cl	—	—	—	—	isocyanuric acid, NaOH, Δ	[8]
			β-Aminoalcohols				
OH	NH_2, NHR^1	$COCl_2$	Cl	Cl	—	—	[9]
OH	NHR^1	$(C_2H_5O)_2CO$	OC_2H_5	OC_2H_5	—	bases	[10]
OH	NHR^1	ethylene carbonate	—	—	OC_2H_4O	—	[11]
OH	NHR^1	$ClCOOC_2H_5$	Cl	OC_2H_5	—	bases	[12]
OH	NHR^1	$(H_2N)_2CO$	NH_2	NH_2	—	—	[13]
OH	NHR^1	RNCO	—	—	NR	—	[14]
OH	NHR^1	Cl_3COOR	CCl_3	OR	—	$R=CH_3$, C_2H_5	[15]
OH	NHR^1	$ClCO_2CH_3$	Cl	OCH_3	—	CS_2	[16]
OH	NHR^1	CO_2	—	—	O	Δ, P	[17]
OH	NHR^1				—	—	[18]
OH	NHR^1	COS	—	—	S	—	[19]
OH	NHR^1	$CO + S$	—	—	—	—	[20]
OH	NHR^1	—	—	—	—	CCl_4	[21]
OH	NHR^1	—	—	—	—	$BrCN + OH$	[22]
OH	NHR^1	$CO + Se$	—	—	—	$(C_2H_5)_3N$	[23—25]
OH	NHR^1	$CH_3COCH_2COOC_2H_5$	CH_2COCH_3	OC_2H_5	—	bases	[26]
			1,2-Glycols				
OH	OH	$(H_2N)_2CO$	NH_2	NH_2	—	—	[27]
OH	OH	$C_2H_5OCONH_2$	OC_2H_5	NH_2	—	bases	[28]
			Acetylene derivatives				
OH	≡CH	R^1NCO	—	—	NR^1	CH_3ONa	[29]
OH	≡CH	$CO_2 + R^1NH_2$	—	—	O	copper salts	[30]
≡CH	NHR^1	CO_2	—	—	O	—	[31]
			β-Hydroxyisocyanates				
OH	NCO	—	—	—	—	—	[3, 32, 33]
			Urethanes				
Cl, Br, I, NH_2	NR^1COOR	—	—	—	—	Δ or OH	[34]
OH	NHCOOR	—	—	—	—	SO_2Cl, P_2O_5	[35]
			α-Ketols				
OH	=O	R^1NCO	—	—	NR^1	—	[36]
OH	=O	$(NH_4)_2CO_3$	ONH_4	ONH_4	—	KCN	[37]
			α-Aminoketones				
=O	NH_2	CO_2	—	—	O	—	[38]
			β-Aminoethyl diphenylphosphate				
$OPO(PhO)_2$	NH_2	CO_2	—	—	O	—	[39]

(a) The Synthesis of 2-Oxazolidinones from 2-Dioxolans

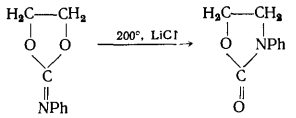
The synthesis of 2-oxazolidinones by the reaction of 2-dioxolans (cyclic carbonates) with isocyanates has been described. Tertiary amines[45], lithium, zinc, and tin chlorides, potassium and sodium carbonates, and sodium hydroxide[46] have been used as catalysts of this reaction. It has been suggested[45] that a molecular complex of the isocyanate and the carbonate is formed as an intermediate, which has been isolated and proved to have a distinct melting point. On heating, this complex decomposed with evolution of carbon dioxide and formation of 2-oxazolidinone. When the reaction of 2-dioxolans with isocyanates was carried out at elevated temperatures, the formation of the complex was not observed.

Substituted 2-oxazolidinones have been obtained by the reaction of cyclic carbonates with formamide[47].

Gulbins and Hamann[48] synthesised 2-oxazolidinones by the reaction of 2-dioxolans with aromatic amines using lithium chloride or alkali (NaOH, KOH) as the catalyst:

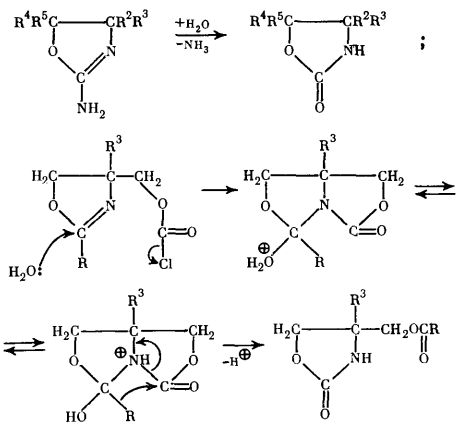


The preparation of oxazolidinones by the reaction of cyclic carbonates with diacylureas[49] and with ammonium carbonate and potassium cyanide[50] and also by the rearrangement of 2-amino-1,3-dioxolans under the influence of lithium chloride[51]:



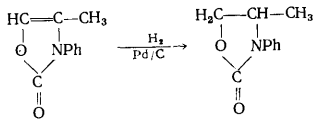
(b) The Synthesis of 2-Oxazolidinones from Oxazolines, Oxazolinones, and Imino-oxazolidinones

2-Oxazolidinones have been obtained by the hydrolysis of 2-amino- and 2-alkyl-2-oxazolines in accordance with the scheme[52,53]

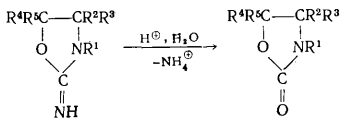


The syntheses of 2-oxazolidinones by the rearrangement of 2-alkoxy-2-oxazolines in inert solvents in the presence of catalytic amounts of alkyl halides have been described in patents[54,55].

The reaction involving the reduction of oxazolinones by hydrogen at atmospheric pressure and room temperature in the presence of a palladium catalyst[56], i.e.



and the hydrolysis of 2-imino-oxazolidones[57], i.e.



belong to methods of synthesis of 2-oxazolidinones without the cleavage of the initial ring.

(c) The Synthesis of 2-Oxazolidinones by the Cleavage of Nitrogen-Containing Heterocycles

The preparation of 4-methyl-2-oxazolidinones by the reaction of propyleneimine with carbon dioxide has been described; polypropyleneimine and polyurethane are formed as side products[58].

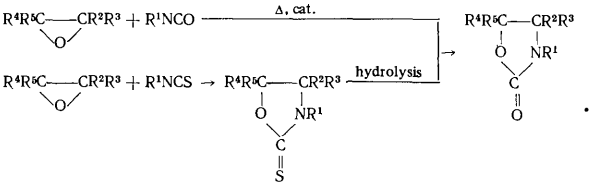
Ikeda and Soga[59] obtained 2-oxazolidinone by the reaction of aziridines having the general formula $\overline{CH_2-CHR^2-NR^1}$ with carbon dioxide; the reaction proceeds in the presence of Lewis acids ($ZnCl_2$, $AlCl_3$) at 60 °C in the course of 50 h.

3. The Reactions of Epoxides with Various Compounds

As mentioned above, one of the most important and promising methods of synthesis of 2-oxazolidinones involves the reactions of epoxides with various compounds (particularly isocyanates), since the initial reactants are in this instance substances produced industrially on a large scale.

(a) The Reactions of Epoxides with Isocyanates and Isothiocyanates

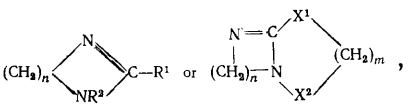
Numerous studies[1,60-77] devoted to the synthesis of 2-oxazolidinones by the reactions of epoxides with organic isocyanates and isothiocyanates have been published. However, there is as yet no unanimous view in the literature concerning either the reaction products or the reaction mechanism. The formation of 2-oxazolidinones can be represented schematically in a general form as follows:



(1)

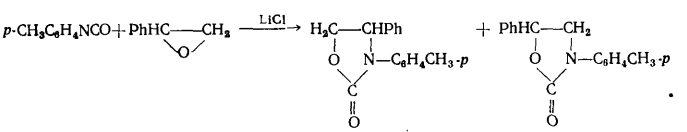
The reaction takes place at elevated temperatures in solvents such as dimethylformamide (DMF), acetonitrile, dioxan[1], and benzene[60] or in the absence of solvents[61], in the presence or absence of catalysts. Secondary[62] and tertiary[63] amines, quaternary ammonium halides[61,64], carboxylate anions[65], zinc, iron[60], and lithium[66] chlorides, the lithium bromide–tributylphosphine oxide complex (or hexamethylphosphoramide),[67] the complexes of aluminium, zinc, and iron halides with ethers, amines, amides, sulphoxides, and phosphines[68], organic derivatives of zinc [R_2Zn and $Zn(OCOR)_2$] and aluminium (AlR_3), with R = alkyl,[69] and Group IIA and IIIA metal alkoxides and phenoxides[70] are used as catalysts. A method of synthesis of oxazolidinones by the reaction of isocyanates with epoxides in the presence of catalysts comprising phosphonium compounds of the type $[R(R^1)(R^2)(R^3)P]^+X^-$, where R^1, R^2 = C_{1-25} alkyl or substituted alkyl, R^3 = alkyl, substituted alkyl, aryl, or substituted aryl, and X = anion of an inorganic or lower aliphatic carboxylic acid [for example, $(n\text{-}C_4H_9)_4PBr$] and with primary and secondary alcohols as cocatalysts has been proposed in a patent[71].

Cyclic amidines having the general formula

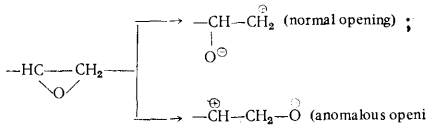


where R^1, R^2 = H, pentyl, or C_{1-8}, X^1, X^2 = alkylene, n = 2–6, and m = 2–11, and their salts have been suggested as catalysts in the synthesis of oxazolidinones[72].

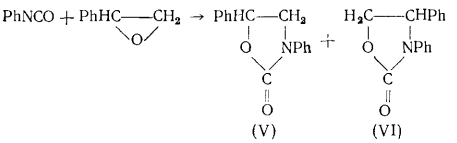
The interaction of isocyanates and epoxides has been investigated[65] in the presence of LiCl as the catalyst. It was found that the reaction results in the formation of a mixture of 3,5- and 3,4-substituted 2-oxazolidinones in proportions of 4 : 1 (by weight):



The formation of two isomers in this reaction is explained by the fact that various ways of opening the epoxide ring are possible:



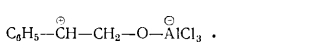
The formation of a mixture of isomers in the reaction of phenyl isocyanate with 2-phenyloxiran (styrene oxide) has been mentioned[73]:



(2)

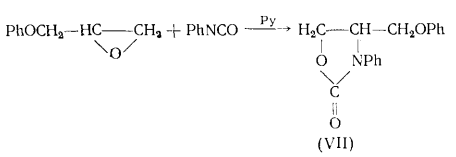
(V) (VI)

It has been established[74] that the reaction of 2-phenyloxiran with phenyl isocyanate in the presence of $AlCl_3$ as the catalyst leads to the formation of a mixture of 3,5-diphenyl-2-oxazolidinone (V) and 3,4-diphenyl-2-oxazolidinone (VI) in proportions of 2:1 [see reaction (2)]. The reaction apparently proceeds preferentially via the formation of the intermediate complex



When $Ca(OC_2H_5)_2$ was used as the catalyst, the formation of only the 3,5-isomer was noted. The authors[74] separated the isomers by fractional crystallisation. They also described[74] the synthesis of various bisoxazolidinones.

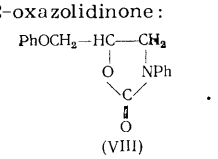
The reaction of glycidyl phenyl ether with phenyl isocyanate in the presence of pyridine (Py) has been investigated[63]:



(3)

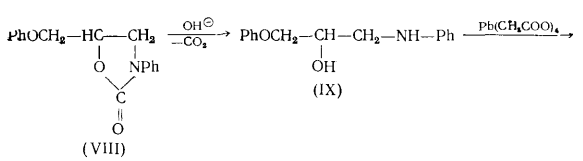
(VII)

The authors[63] concluded that the reaction results in the formation of 4-phenoxymethyl-3-phenyl-2-oxazolidinone (VII), while other workers[60,75] noted that, when the process is carried out under anomalous conditions, the product is 5-phenoxymethyl-3-phenyl-2-oxazolidinone:

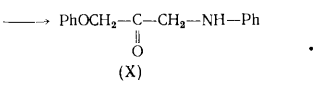


(VIII)

Braun and Weinert[10] also described the synthesis of 5-phenoxymethyl-3-phenyl-2-oxazolidinone (VIII) by reaction (3) in a high yield. Pyridine as well as metal alkoxides and chlorides and $(CH_3)_4Ni$ were used as the catalysts. In order to demonstrate the structure of the resulting 2-oxazolidinone, the authors[10] hydrolysed it. Evidently the hydrolysis of 5-phenoxymethyl-3-phenyl-2-oxazolidinone (VIII) should result in the formation of the secondary alcohol 1-phenoxy-3-phenylamino-2-propanol (IX), which yields the corresponding ketone (X) on oxidation with lead tetra-acetate:

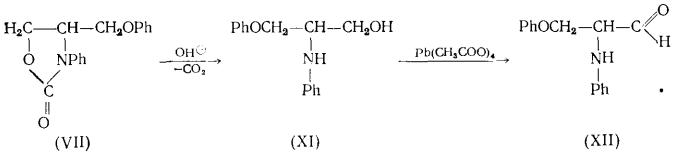


(VIII) (IX)



(X)

The hydrolysis of 4-phenoxymethyl-3-phenyl-2-oxazolidinone results in the formation of the primary alcohol 3-phenoxy-2-phenylamino-1-propanol (XI), which can be oxidised to the aldehyde (XII) by lead tetra-acetate:

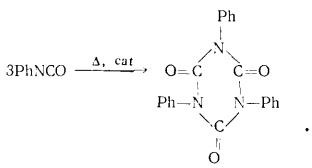


(VII) (XI) (XII)

The infrared spectra of the products of hydrolysis and subsequent oxidation confirmed that the reaction of glycidyl phenyl ether with phenyl isocyanate in the presence of all the catalysts tested (see above) leads to the formation of 5-phenoxymethyl-3-phenyl-2-oxazolidinone (VIII).

Thus inspection of the literature data permits the conclusion that the views of different workers concerning the isomeric products of the reaction of epoxides with isocyanates are extremely contradictory. As a rule the mode of opening of the epoxide ring and hence the formation of a particular isomeric 2-oxazolidinone depend on the catalyst employed and on the nature of the substituent in the epoxide.

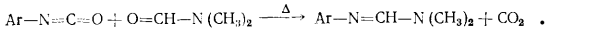
Sandler et al.[61] investigated the relative contributions of the two competing reactions involving the formation of the oxazolidinone [see Scheme (3)] and the cyclotrimerisation of phenyl isocyanate:



(4)

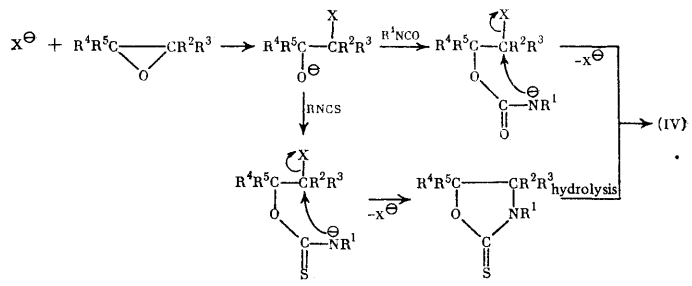
The reaction was carried out in the presence of $(CH_3)_4Ni$ as the catalyst in DMF. The authors[51] showed that oxazolidinone formation reactions take place preferentially in accordance with Eqn.(3) at 140–160 °C, while at 56 °C triphenyl isocyanurate is formed in accordance with reaction (4).

The reaction of epoxides with isocyanates has been carried out in a number of investigations[51,66] in DMF. However, according to Weiner[76], aryl isocyanates react with DMF at an elevated temperature to form formamidines:

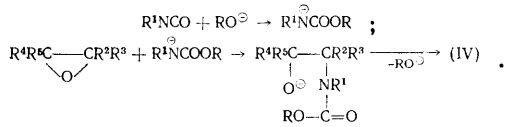


However, Sandler[61] did not point out the possibility of this side reaction. In order to eliminate it, Herweh et al.[66] added the isocyanate to a solution, heated under a reflux condenser, of the epoxide and the catalyst [$(CH_3)_4Ni$ or LiCl] in DMF. However, in the present author's view, this cannot prevent the reaction of the isocyanate with DMF.

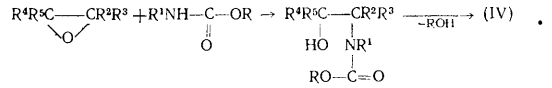
The nature of the catalyst influences the mechanism of the reaction of epoxides with isocyanates. Thus it has been suggested[1] that in the presence of metal halides the epoxide adds directly to the isocyanate (or isothiocyanate) with formation of an activated complex via the reaction



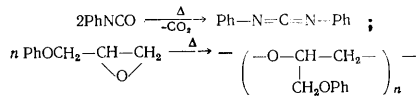
It has been established[77] that, in the presence of alkaline earth metal alkoxides, there is no reaction between the epoxide and the alkoxide and also between the epoxide and the isocyanate. It has therefore been suggested that the oxazolidinone is formed via a stage involving the interaction of the isocyanate with the alkoxide anion followed by the condensation of the urethane anion and the liberation of the alkoxide anion in accordance with the reaction



It has been shown[75] that the formation of oxazolidinones in the presence of quaternary ammonium salts takes place only in the presence of small amounts of an alcohol. Hence, it is believed[75] that oxazolidinones are formed via the condensation of the urethane with the epoxide with liberation of an alcohol and the closure of the oxazolidinone ring. According to the authors[75], the quaternary ammonium salts play the role of compounds which enhance the nucleophilic properties of the urethane nitrogen. The reaction proceeds as follows:



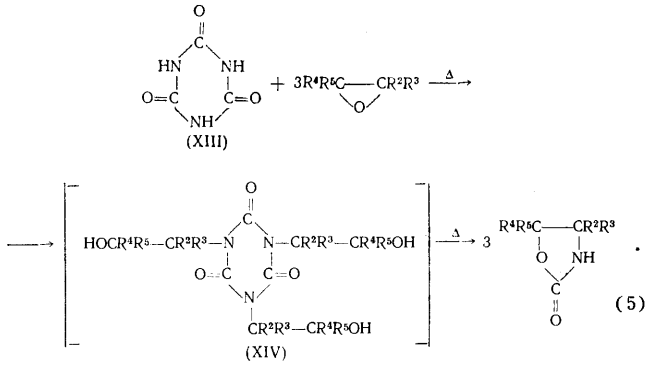
One should note that the reaction of epoxides with isocyanates in the absence of catalysts and solvents has been mentioned in the literature. Thus 5-phenoxymethyl-3-phenyl-2-oxazolidinone has been obtained[61] by heating a mixture of equivalent amounts of phenyl isocyanate and glycidyl phenyl ether at 210 °C for 15 h. Evidently in the absence of a catalyst of the oxazolidinone formation reaction, side reactions occur in the given system, namely the cyclotrimerisation of phenyl isocyanate [see reaction (4)] and also the conversion of phenyl isocyanate into a carbodiimide and linear polymerisation of glycidyl phenyl ether:



(b) The Reaction of Epoxides with Isocyanurates

Since one of the main side processes in the reaction of epoxides with isocyanates involves the formation of isocyanurates, studies on the interaction of the latter with epoxides are of undoubted interest. Thus it has been found in a number of investigations[78–80] that, on treatment with epoxides, the stable isocyanurate ring decomposes with formation of a 2-oxazolidinone.

The reaction of epoxyethane and other epoxides with isocyanuric acid (XIII) has been investigated[78–79]. It has been shown[79] that the reaction proceeds as follows:

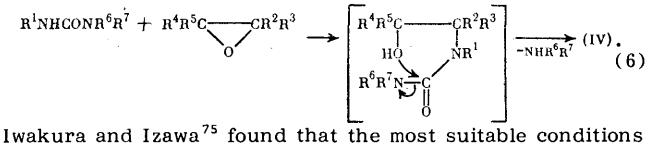


It was carried out in DMF or dimethylacetamide at 100 °C and atmospheric pressure. Pyrolysis of the tris(hydroxyalkyl) isocyanurate (XIV) *in vacuo* at 200 °C or on heating in DMF (150–155 °C) leads to the corresponding 2-oxazolidinone [reaction (5)].

Korshak et al.[80] investigated the reaction of glycidyl phenyl ether and triphenyl isocyanurate in molar proportions of 3:1 (at 230 °C for 10 h) and showed that the only product is 5-phenoxymethyl-3-phenyl-2-oxazolidinone.

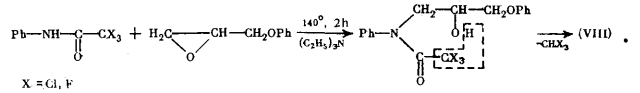
(c) The Reactions of Epoxides with Ureas, Amides, and Urethanes

Apart from their reactions with isocyanates, isothiocyanates, and isocyanurates, epoxides are capable of cleaving the urea, amide, and urethane linkages with formation of 2-oxazolidinones. Thus the reaction of epoxides with urea derivatives to give 2-oxazolidinones has been reported[75–81]:

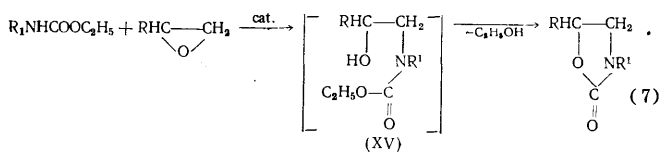


Iwakura and Izawa[75] found that the most suitable conditions for the reactions of di- and tri-substituted ureas with epoxycompounds [see reaction (6)] are a temperature of 90 °C, the absence of a solvent, and the presence of the $(C_2H_5)_3N$ catalyst. A two- or threefold excess of the epoxide is also necessary, since the primary or secondary amines formed rapidly react with epoxides. It is noteworthy that *N*-aryl-*N*,*N*'-disubstituted ureas give rise to oxazolidinones, while *N*-alkyl-*N*,*N*'-disubstituted ureas do not form such compounds.

The same investigators[82,83] studied the interaction of epoxides with acid amides. In particular they studied the reaction of acetanilide and its derivatives with glycidyl phenyl ether and showed that 2-oxazolidinones are formed only from trifluoro- and trichloro-acetanilides, which indicates the necessity for the presence of strong electron-accepting substituents in the acetanilide molecules for the cyclisation to occur:



Urethanes react with epoxides to form oxazolidinones in the presence of nucleophilic catalysts such as KOH,[6] tertiary amines, and quaternary ammonium salts[75]:

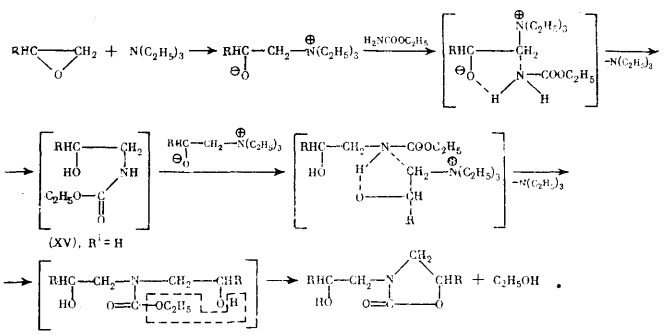


(7)

It has been observed[97] that without a catalyst reaction (7) between a urethane and an epoxide does not take place. When the mixture of the initial components is heated from 0° to 200 °C, only the homopolymerisation of the epoxide is observed. In the presence of $(C_2H_5)_3N$ at 25 °C the reaction takes place quantitatively in 2 h. At 140 °C the reaction terminates after 2–3 min (side reactions were not observed).

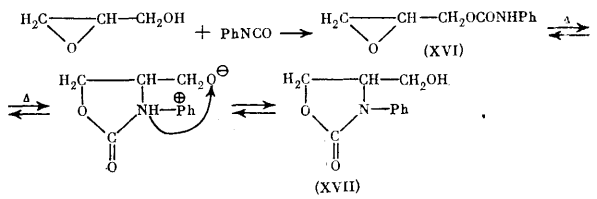
The authors[75] showed that in the presence of solvents (ethanol, benzene, toluene, chloroform and DMF) the reaction occurs at a higher rate than in bulk. *N*-Arylurethanes and *N,N'*-difunctional arylurethanes form oxalidinones on interaction with epoxides, while *N*-alkylurethanes do not undergo the oxazolidinone formation reaction with epoxides (like *N*-alkylureas—see above). According to the mechanism proposed[75], the catalyst is involved in the opening of the epoxide ring and reacts with the epoxide to form an intermediate complex, which then interacts with the urethane; this entails the formation of *N*-(β-hydroxyethyl)urethane (XV), which cyclises with elimination of an alcohol and the formation of a 2-oxazolidinone (IV).

The kinetics of the reaction of an epoxide with *N*-unsubstituted ethylurethane in the presence of $(C_2H_5)_3N$ as the catalyst have been investigated[84]. The mechanism proposed[84] is similar to that described above[75], but the authors[84] believe that the *N*-(β-hydroxyethyl)urethane (XV, R' = H) formed reacts with yet another molecule of the adduct of the epoxide and triethylamine which results in the formation of a hydroxy-2-oxazolidinone:

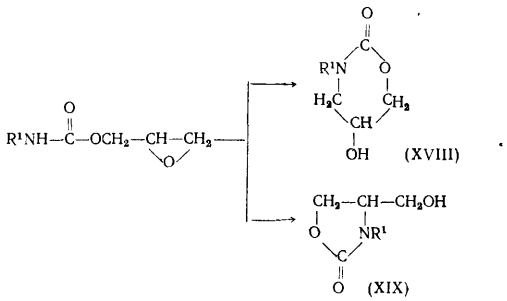


(d) Intramolecular Cyclisation of Glycidyl Esters of *N*-substituted Carbamic Acids

The glycidyl esters of *N*-substituted carbamic acids undergo intramolecular cyclisation on heating with formation of 2-oxazolidinone derivatives. Thus the reaction of phenyl isocyanates with glycidol results in the formation of glycidyl *N*-phenylcarbamate (XVI), which is converted on heating into 4-hydroxymethyl-3-phenyl-2-oxazolidinone (XVII):[85]



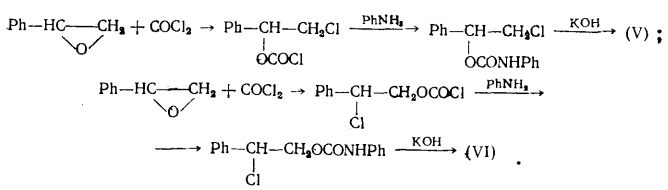
^{1}H NMR spectra[74,85] confirm the location of the hydroxymethyl group in compound (XVII) at the carbon atom adjoining the nitrogen atom of the oxazolidinone ring. However, hitherto there has been no definite view concerning the structure of the cyclisation products. Thus the formation of the six-membered 2-oxazinone ring (XVIII) has been postulated[86], while according to other data[85] the five-membered 2-oxazolidinone ring (XIX) is produced:



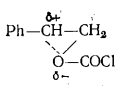
Sorokin and co-workers investigated in a series of studies in recent years[87–92] the intramolecular cyclisation of glycidylurethanes and demonstrated the formation of a five-membered structure (XIX). They showed[87–92] that in proton-donating solvents the reaction takes place at lower temperatures (100 to 140 °C) than in neutral solvents (170–200 °C). Tertiary amines are active cyclisation catalysts. The equality of the molecular weights of the resulting product and of the initial glycidylurethane, the absence of epoxy-groups, and the appearance of hydroxy-groups in an amount corresponding to the cyclisation product indicates the absence of side reactions and the quantitative interaction of the epoxide and urethane groups to form the cyclic compound (XVIII) or (XIX). In order to demonstrate the structure, a study was made[92] of the ^{1}H NMR spectra of the reaction product and it was shown that the signals of the protons in the epoxide and urethane groups are absent and that the signal due to the OH group with δ = 5.2 p.p.m. appears. Its triplet form shows that the hydroxy-group is primary and not secondary and that anomalous opening of the epoxide ring therefore takes place (see above) and the cyclisation product is the five-membered 2-oxazolidinone ring (XIX).

(e) The Interaction of Epoxides with Other Compounds

Irwin and Wheeler[73] investigated the successive interaction of 2-phenyloxiran with phosgene, aniline, and KOH. Two reaction pathways are possible; the products are 3,5-diphenyl-2-oxazolidinone and 3,4-diphenyl-2-oxazolidinone respectively:

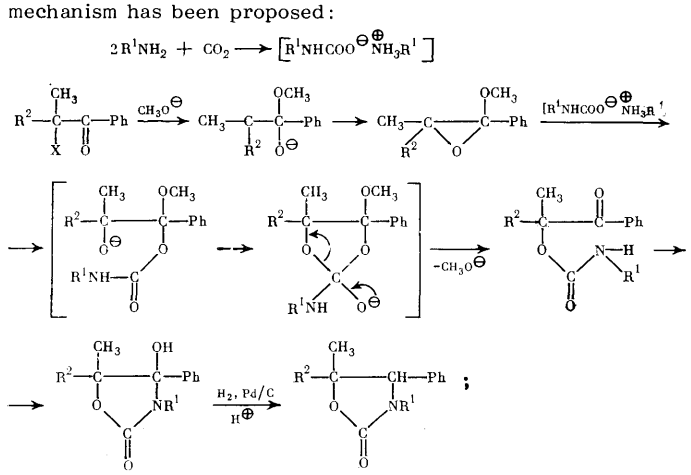


The authors[73] concluded that the oxazolidinone is formed via an intermediate complex:



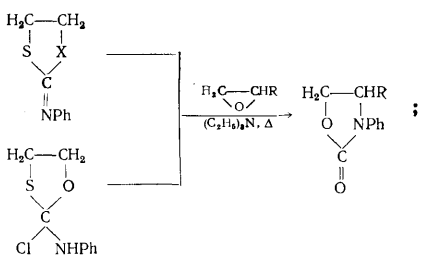
The ^1H NMR spectra confirmed that 3,5-diphenyl-2-oxazolidinone is the main reaction product.

The reactions of 2-methoxyoxirans and of α-halogeno-derivatives of acylphenones with carbon dioxide in aliphatic amines in methanol have been studied[36] and the following reaction mechanism has been proposed:



X = Br, Cl; R^1 = alkyl ; R^2 = CH_3, H .

A series of syntheses of 2-oxazolidinones from epoxides and five-membered heterocycles containing oxygen and sulphur in various combinations have been achieved[93]:



X=O, S; R=H, CH_3, CH_2Cl .

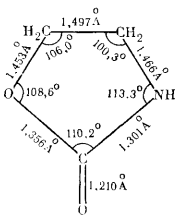
Substituted oxazolidinones have been synthesised[94] by the reaction of epoxides with compounds of the type p-RC_6H_4N = CCl_2 in the presence of $ZnCl_2$ or $SnCl_2$ as catalysts.

III. THE PROPERTIES OF 2-OXAZOLIDINONES

1. The Physical Properties of 2-Oxazolidinones

2-Oxazolidinones are stable heterocyclic compounds whose melting points are in most cases in the range 100–200 °C;[95,96] they are soluble in water and form neutral solutions.

The polymorphism and the mechanochemistry of 5-phenoxymethyl-2-oxazolidinone have been investigated[97] and it has been observed that the oxazolidinone exhibits dimorphism, existing in two independent forms or their mixture.



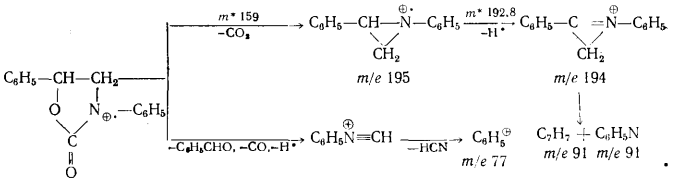
The crystal structure of 2-oxazolidinone

The crystal structure of 2-oxazolidinone has been described[98]. It has a monoclinic three-dimensional crystal lattice with the unit cell dimensions a = 7.313 Å, b = 5.672 Å, c = 9.970 Å, and β = 110.78° (measured at 24 °C). The bond lengths and the angles in the ring are shown in the Figure above.

The infrared spectra of 2-oxazolidinones have been investigated in a number of studies[99–102]. The carbonyl absorption of 2-oxazolidinones is observed in the range 1740–1810 cm^{-1} (usually at 1740–1760 cm^{-1}). 2-Oxazolidinones with an unsubstituted hydrogen atom at the nitrogen atom show an absorption by the N–H group in the range 3200–3500 cm^{-1}.[100]

Several detailed studies on the NMR of 2-oxazolidinones have been made[66,103].

Disubstituted mono- and bis-2-oxazolidinones have been investigated mass-spectrometrically[73,104] and it has been shown that the decomposition of 5-alkyl-, 4-alkyl-, 5-aryl-, and 4-aryl-3-phenyl-2-oxazolidinones takes place as follows: (1) with evolution of CO_2 on β-decomposition; (2) with evolution of CO and the formation of the corresponding aldehyde on α-decomposition. The intense *m/e* 194 peak in the mass spectrum of 5-aryl(or alkyl)-3-phenyl-2-oxazolidinone, characterising the decomposition with evolution of Cl_2, is almost completely absent from the spectrum of 4-aryl(or alkyl)-3-phenyl-2-oxazolidinone, a characteristic feature of which is the cleavage reaction with evolution of CO and the formation of the corresponding aldehyde. For example, the decomposition of 3,5-diphenyl-2-oxazolidinone under the influence of β-irradiation proceeds in accordance with the following scheme:



The dipole moments of 2-oxazolidinones have been published[105] and it has been concluded that the dipolar structure makes a contribution of approximately 21% to the experimental dipole moment (5.04 ± 0.005 D).

Lebedev and Yakshimets[106] investigated the magnetic susceptibility of 2-oxazolidinone and established that the substance is diamagnetic.

Volumetric titration with silver nitrate, spectrophotometry[107,108], calorimetry[107,109], reaction with indole[110], chromatography[107], and methods based on the formation of a phenylhydrazone[111] have been suggested as methods whereby 2-oxazolidinones can be characterised.

2. The Chemical Properties of 2-Oxazolidinones

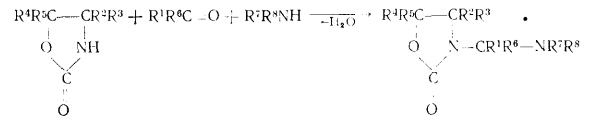
A number of studies have been made on the chemical properties of 2-oxazolidinones. The reactions of 2-oxazolidinones can be divided into the following groups: (a) reactions involving substitution at the ring atoms; (b) ring opening reactions; (c) other reactions involving the ring; (d) reactions of the substituents.

Only the first three groups of reactions, which characterise directly the chemical properties of the oxazolidinone ring, are discussed below.

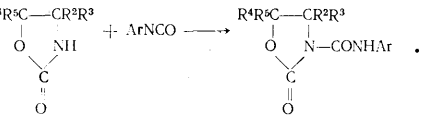
(a) Reactions involving Substitution at the Atoms of the 2-Oxazolidinone Ring

The hydrogen atom linked to the nitrogen atom of the oxazolidinone ring can be substituted by various groups using the following procedures: by reaction with carbonyl compounds, aryl isocyanates, and phosphorus compounds, by alkylation, acylation, carbamoylation, nitration, and amination, by reaction with nitrous acid, etc.

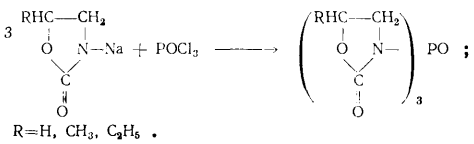
2-Oxazolidinones react with carbonyl compounds in the presence of secondary amines[112]. In the absence of an amine, a second oxazolidinone molecule behaves as an amine (R″R‴NH = $OCOCH_2CH_2NH$). The reaction proceeds as follows:



2-Oxazolidinone-3-carbanilides can be obtained by the reaction of substituted 2-oxazolidinones with aryl isocyanates in the presence of pyridine or triethylamine[113]:

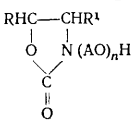


Sodio-derivatives of 2-oxazolidinones react with phosphoryl chloride in DMF in a stream of nitrogen[114]:



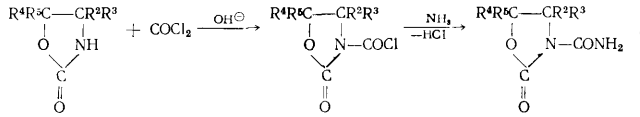
Alkylation is usually carried out in the presence of K_2CO_3, NaOH, CH_3ONa, NaH, and other bases[115]. Organic halides[115,116], olefins[117], and ethers together with benzoic acid and mercury acetate[117] have been proposed as alkylating agents.

The synthesis of a compound having the general formula



(R, R^1 = H, alkyl, or phenyl; AO = C_2–C_5 alkylene oxide group; n = 1–25) by treating 1 mole of 2-oxazolidinone with n moles of an alkylene oxide in the presence of 0.1–10% of a strong basic catalyst (alkali metal hydroxide, sodium salt of 2-oxazolidinone, or a quaternary base) at 90–180 °C and a pressure of 2–10 atm for 2–4 h has been described in a patent[118].

The nitrogen atom has been acylated in alkaline and acid media[119] and carbamoylation has been carried out by treating 2-oxazolidinone with phosgene in an alkaline medium followed by reaction with ammonia[120]:

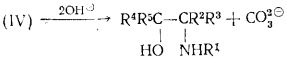


The substitution of the hydrogen atom at the nitrogen atom of the oxazolidinone ring by the NO group has been achieved by the reaction of 2-oxazolidinone with HNO_2 or NOCl.[121]

The nitration of 2-oxazolidinone has been performed by treatment with a mixture of nitric and sulphuric acids or nitric acid and acetic anhydride[122]. The nitro-group can be reduced to the amino-group electrolytically, by hydrogenation in the presence of platinum oxide in an acid medium, or by reaction with zinc and hydrochloric acid[121].

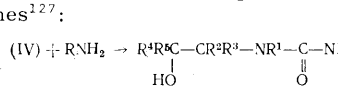
(b) Reactions involving the Opening of the 2-Oxazolidinone Ring

Alkaline hydrolysis of 2-oxazolidinones leads to β-aminoalcohols. It takes place in aqueous[57,116,123] and alcoholic[124] media and in dioxan[125]. It is usually employed to demonstrate the structure and stereochemistry of oxazolidinones[27,37,124,125]. The catalytic conversion of 2-oxazolidinone into the corresponding aminoalcohols by heating the initial compound at 105–200 °C in the presence of bases such as NaOH, KOH, Na_2CO_3, K_2CO_3, and $NaHCO_3$ has been achieved[126]. The reaction takes place in accordance with the following scheme:

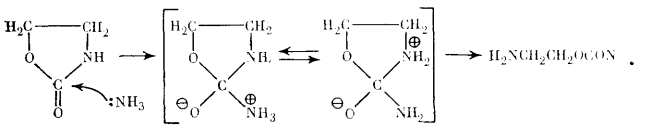


β-Aminoalcohols are also formed on reduction of 2-oxazolidinones with lithium tetrahydroaluminate[27].

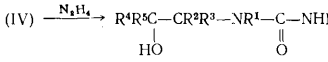
N,*N*′-Disubstituted ureas are the main products of the reaction of 2-oxazolidinones with equimolar amounts of primary aliphatic amines[127]:



2-Oxazolidinone reacts with aqueous ammonia to form β-aminoethyl carbamate[128]:

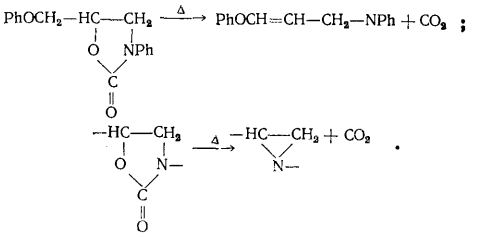


The reaction of 2-oxazolidinones with hydrazine leads to semicarbazides[129]:



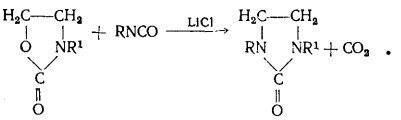
Acid hydrolysis (with concentrated or diluted hydrochloric acid) leads to the formation of the hydrochlorides of β-aminoalcohols[130], while the reaction of 2-oxazolidinone with anhydrous hydrogen chloride results in the formation of β-chloroamine hydrochloride[131].

The thermal stability, the kinetics of the initial stage of the thermal decomposition, and the main decomposition products of 2-oxazolidinones have been investigated[132–134]. It has been shown[133] that heating of 2-oxazolidinones in the absence of air and water is accompanied by autocatalytic decomposition with evolution of CO_2 as the main gaseous reaction product. It was noted that 2-oxazolidinones with alicyclic substituents at the ring nitrogen atom have a higher thermal stability than 2-oxazolidinones with aromatic substituents. Comparison[134] of the thermal stabilities of isocyanurates, oxazolidinones, and carbamates showed that compounds of these classes can be arranged in the following sequence in terms of their thermal stabilities: carbamates < oxazolidinones < isocyanurates. The thermal decomposition of 5-phenoxymethyl-3-phenyl-2-oxazolidinone results in the formation of PhOH, $PhNH_2$, H_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_6 + C_3H_8, and a C_4 fraction. The formation of the possible intermediate thermolysis products is illustrated schematically below:

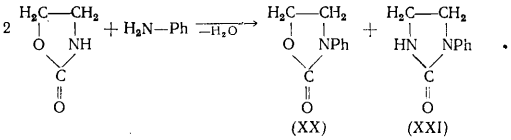


(c) Other Reactions involving the 2-Oxazolidinone Ring

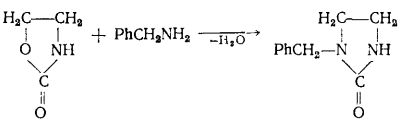
The reaction of *N*-substituted 2-oxazolidinones with organic isocyanates in the presence of lithium chloride leads to *N*,*N*'-disubstituted 2-imidazolidinones[135]:



It has been noted[136] that the reaction of 2-oxazolidinone with aniline results in the formation of water, 3-phenyl-2-oxazolidinone (XX), and 1-phenyl-2-imidazolidinone (XXI):



The synthesis of 1-benzyl-2-imidazolidinone from 2-oxazolidinone and benzylamine has been described[137]:



IV. THE SYNTHESIS, PROPERTIES, AND APPLICATIONS OF POLYMERS CONTAINING 2-OXAZOLIDINONE RINGS

One of the most important practical applications of 2-oxazolidinones involves the synthesis of polymers containing 2-oxazolidinone rings; recently these polymers have found applications in the preparation of thermostable and heat-resistant foams, coatings, adhesives, fibres, and electrically insulating materials with effective physicomechanical properties.

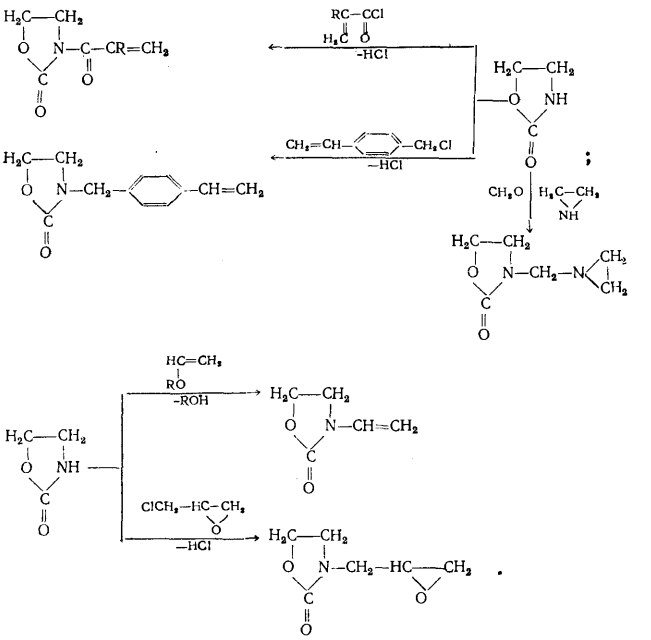
There are virtually no reviews in the Soviet and foreign literature on polymers with oxazolidinone ring. In this section of the present review we shall therefore examine the available information about the synthesis, reaction mechanisms, properties, and applications of polymers in this practically important class.

Numerous methods of synthesis of polymers whose structure incorporates 2-oxazolidinone rings have been described. It is possible to distinguish two fundamentally different types of synthesis of polyoxazolidinones: the first involves the synthesis of the polymers from monomers containing complete 2-oxazolidinone rings in their structure, while in the second the 2-oxazolidinone rings are formed in the course of the synthesis of the polymer. In the former case the products are polymers whose 2-oxazolidinone rings are in a side chain while in the latter case they are in the main chain. They will be examined below in the same order.

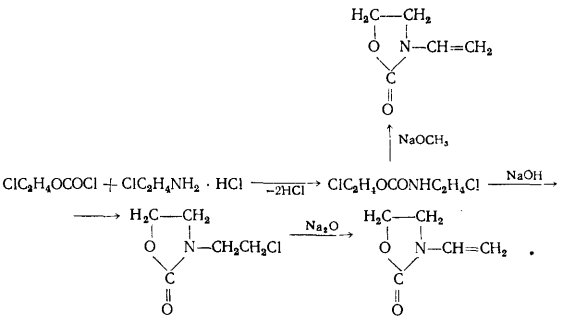
1. Polymers Containing 2-Oxazolidinone Rings in a Side Chain

Polyoxazolidinones based on monomers incorporating complete 2-oxazolidinone rings can be obtained in several ways and contain these rings in a side chain and at the ends of the macromolecules.

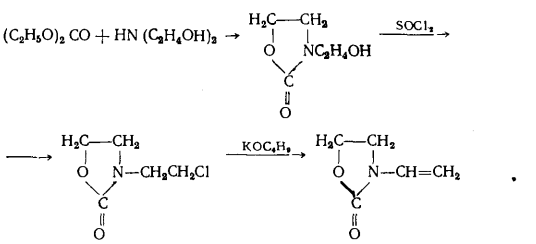
The initial monomers for the synthesis of polyoxazolidinones with side or terminal 2-oxazolidinone rings are obtained by substituting the hydrogen at the nitrogen atom of the oxazolidinone ring by groups capable of polymerisation. A series of syntheses of such monomers are shown schematically below:



The following method of synthesis of *N*-vinyl-2-oxazolidinone has been proposed[138]:

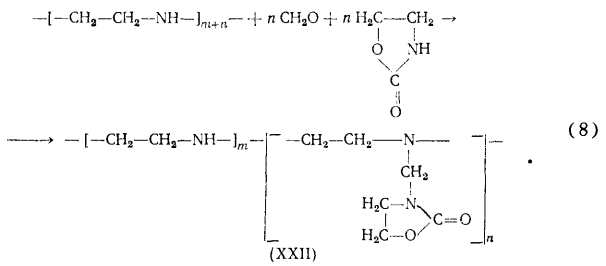


Drechsel[139] obtained *N*-vinyl-2-oxazolidinone by the following procedure:



N-Vinyl-2-oxazolidinones[33,140-142], *N*-isopropenyl-2-oxazolidinones[143], *N*-allyl-2-oxazolidinones[144], 5-methylene-2-oxazolidinones[31], and other 2-oxazolidinones containing unsaturated bonds enter into radical homopolymerisation and copolymerisation reactions with various vinyl and other monomers, such as *N*-vinyl-2-pyrrolidinone[145], *N*,*N*',*N*''-triphenyl-*B*,*B*',*B*''-trivinylborazole[146], maleic anhydride[147], isocyanates[148], acrylonitrile, ethyl acrylate, styrene, methyl methacrylate, vinyl acetate, vinylidene chloride, acrylamide, vinyl chloride, decyl methacrylate[141,142,149,150], monovinyl ethers of glycols having the general formula $HO(C_nH_{2n}O)_x$. $.CH=CH_2$, where $n = 2-4$ and $x = 1-3$,[151] and phthalic anhydride[152]. α,α-Azobisisobutyronitrile is usually employed as the polymerisation catalyst. The polymers and copolymers based on monomeric unsaturated 2-oxazolidinones dissolve in *m*-cresol and acetic, formic and dilute hydrochloric acids, but are insoluble in solvents such as ethanol, acetone, and dioxan. They have fairly high softening temperatures (up to 300° and above) and effective physicomechanical properties, which makes it possible to employ them in various branches of engineering (see below).

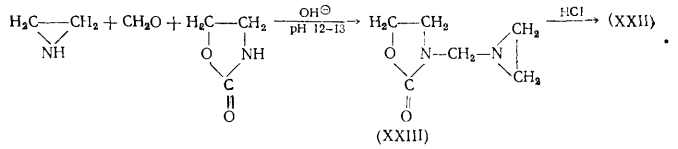
A series of polyethyleneimines containing 2-oxazolidinone rings in the side chains have been synthesised[112] in several ways. The reaction of 2-oxazolidinone with formaldehyde and polyethyleneimine at room temperature in solvents such as water, DMF, and a dioxan–water mixture proceeds in accordance with the following scheme:



(8)

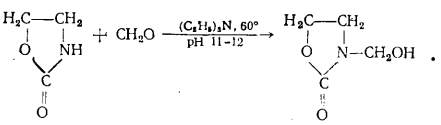
(XXII)

The polymer (XXII) has also been synthesised[112] by the polymerisation of *N*-(1-azirinomethyl)-2-oxazolidinone (XXIII), which had been obtained in its turn from aziridine, formaldehyde, and 2-oxazolidinone:



(XXIII)

In addition, a polymer of type (XXII) had been obtained[112] by the reaction of polyethyleneimine with *N*-hydroxymethyl-2-oxazolidinone in an aqueous medium at room temperature. *N*-Hydroxymethyl-2-oxazolidinone was synthesised from 2-oxazolidinone and formaldehyde by the reaction



The polyethyleneimines described are capable of adsorbing polar substances from aqueous solutions. In an alkaline medium these polymers form complexes with phenol and with toluene-*p*-sulphonic acid; the infrared spectra of the complexes indicate the presence of a hydrogen bond between the CO group of the 2-oxazolidinone ring of the polymer and the hydrogen atom of the phenol or toluene-*p*-sulphonic acid[112].

2. Polymers Containing 2-Oxazolidinone Rings in the Main Chain

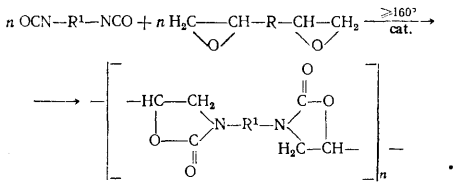
There are literature data on the synthesis and properties of linear, branched, and cross-linked poly-2-oxazolidinones and also polymers containing in their structure other rings and functional groups in addition to the 2-oxazolidinone groups. Studies on the synthesis and properties of linear poly-2-oxazolidinones with 2-oxazolidinone rings in the main chain, hydroxy-2-oxazolidinones, and cross-linked oxazolidinone-isocyanurate polymers are examined below.

(a) Linear Poly-2-oxazolidinones

As mentioned above, one of the most important methods of synthesis of mono- and poly-2-oxazolidinones involves the reaction of epoxides with isocyanates, since these starting materials are readily available industrial products.

Gromakov et al.[153] investigated the reaction of epoxy-resins with di-isocyanates by differential thermal analysis (DTA). The formation of poly-2-oxazolidinones has been observed in the absence of catalysts at temperatures in the range 160 to 250 °C. The same workers[154] investigated by infrared spectroscopy and DTA the reactivities of various epoxy-resins and di-isocyanates. The reactivities of the epoxy-resins increased in the sequence diglycidyl ether of bisphenol A < triglycidyl isocyanurate < diglycidylaniline. The reactivities of the di-isocyanates increase in the sequence 3,3'-dimethyl-4,4'-diphenylmethylene di-isocyanate < 4,4'-diphenylmethylene di-isocyanate < 2,4(2,6)-tolylene di-isocyanate.

High-molecular-weight linear poly-2-oxazolidinones have been synthesised[77] by the slow addition of a di-isocyanate to a solution of a diepoxide and a catalyst (lithium n-butoxide in butanol) in *o*-dichlorobenzene in accordance with the following reaction:



Effective catalysts for the synthesis of elastomeric poly-2-oxazolidinones have been sought in one of the latest studies on the synthesis of linear poly-2-oxazolidinones[155]. The initial di-isocyanate used was polyoxytetramethylene glycol with terminal isocyanate groups and the diepoxide was the diglycidyl ether of bisphenol A. The polymerisation was carried out in bulk. Insoluble catalysts (LiF, $MgCl_2$) proved to be relatively ineffective; the most effective catalysts were the complexes of LiBr, LiCl, LiI, $MgCl_2$ with hexamethylphosphoramide. With increase of temperature from 80° to 150 °C, the yield of the polymer increased by 20%, the reaction occurring over a period of 1 h at 150 °C. The optimum ratio of the initial epoxy-groups and NCO groups is 45 : 55. Hexamethylphosphoramide is a chelating agent, forming coordinate bonds with metal chlorides. In this connection the influence of the coordination number *m* on the polymerisation was discovered and it was shown that $m = 2$ to 4 is preferred. The authors investigated the physicomechanical properties (Young's modulus, tensile strength, relative elongation, tearing energy, the relaxation of stress, and creep) of elastomers containing oxazolidinone and urethane linkages in the main chain. From their results, it was concluded that, together with the high thermally insulating properties of polyester-urethanes and polyoxazolidinones, the polyoxazolidinone has a higher yield point (T_{yield} is 235 to

245 °C for the polyoxazolidinone and 200–220 °C for polyester-urethane) and retains its strength much more effectively after ageing at 170 °C. However, the polyoxazolidinone has a lower strength at a high temperature, while the tearing energy, the relaxation of stress, and creep are virtually at the same level as in polyester-urethane.

Chelate complexes, namely the Mg, Li, Al, Ba, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Hg, Pb, Sn, Be, Mo, and Zr complexes of β-diketones, dimethylglyoxime, salicylaldehyde, α-nitroso-β-naphthol, benzoylacetone, anthranilic acid, etc. have also been proposed in a patent[156] as catalysts of the reaction of polyisocyanates with polyepoxides leading to the formation of oxazolidinones [polyoxazolidinones?]. Complexes of Lewis acids (Al, Zn, and Fe halides) with Lewis bases such as thioesters, amines, (*N*-alkyl)lactams, amides, etc. have been put forward[157–159] as catalysts for the synthesis of polyoxazolidinones.

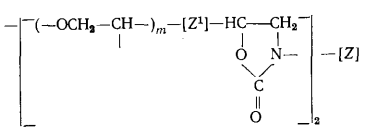
Quaternary ammonium salts of the type $(CH_3)_4NI$, $(C_2H_5)_4NI$, $(CH_3)_4NBr$, and $(C_2H_5)_4NBr$ are very widely used as catalysts of the oxazolidinone formation reaction[160–162].

Linear poly-2-oxazolidinones have been synthesised in DMF in the presence of $(CH_3)_4NI$ at 140–160 °C.[61,64,163]. The possibility of the occurrence of a side reaction of DMF with isocyanates, described by Weiner[76], was not discussed in the above investigations, although it undoubtedly occurs in the given instance.

Herweh and Whitmore[164] synthesised poly-2-oxazolidinones by the 1,3-cycloaddition of diglycidyl ethers and di-isocyanates in the presence of a catalyst (lithium chloride), also in DMF. The reaction was carried out with refluxing in DMF for 12 h. It was found that at 150 °C the side reaction of isocyanates with DMF [76] takes place together with the formation of oxazolidinones. It was noted[164] that the poly-2-oxazolidinones obtained from aromatic di-isocyanates have a lower degree of crystallinity than the polymers obtained from aliphatic di-isocyanates. The authors[164] believe that the amorphous structure of the poly-2-oxazolidinones is due to the irregular structure of the polymer chain and the presence in the latter of isomeric 2-oxazolidinone rings.

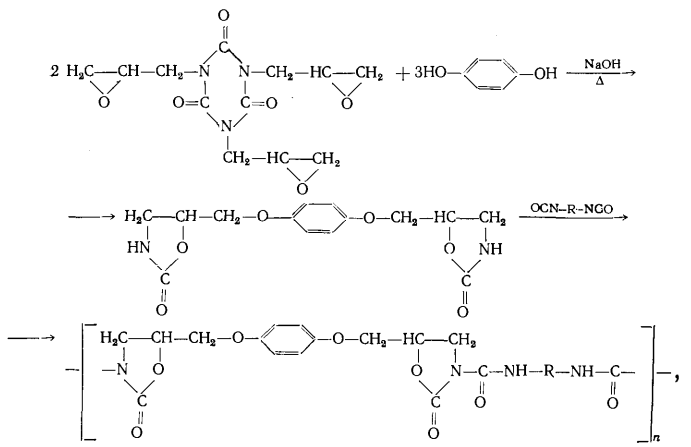
ε-Caprolactam[165], organic compounds of zinc and aluminium[69], cyclic amidines[72], a wide variety of phosphonium compounds[71,166–169], salts of the type BF_3–$C_2H_5NH_2$,[170] tri(ethylaminophenyl) borate[171], and metal compounds containing halogens and the CO_3^{2-}, NO_2^-, ClO_4^-, CN^-, and SCN^- groups with and without neutral ligands[172] have also been proposed as catalysts for the synthesis of poly-2-oxazolidinones.

Novolak epoxy-resins modified by oxazolidinone and having the general formula

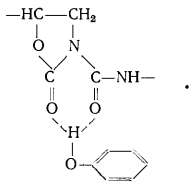


where Z is the organic polyisocyanate residue, Z^1 the epoxy-compound residue, m = 1.5–5.0, have been synthesised[173] by the reaction of polyisocyanates with epoxy-compounds. These polymers are suitable for the preparation of adhesives which are stable under the conditions of high humidity.

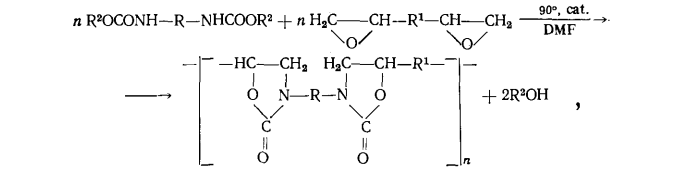
Poly-2-oxazolidinone has been obtained[174] by the reaction of di-isocyanates with bisoxazolidinones in *N*-methylpyrrolidinone at 48 °C in the presence of triethylenediamine. The bisoxazolidinone was obtained by refluxing tris(2,3-epoxypropyl) isocyanurate with hydroquinone in DMF in the presence of NaOH:



where R = alkyl or aryl. The polymers obtained are soluble in *N*-methylpyrrolidinone and *m*-cresol and less so in DMF. The intrinsic viscosities are 0.16–0.64 dl g^{-1} depending on the nature of the di-isocyanate. The presence of the 2-oxazolidinone rings in the polymer is responsible for their ability to form complexes with phenol:



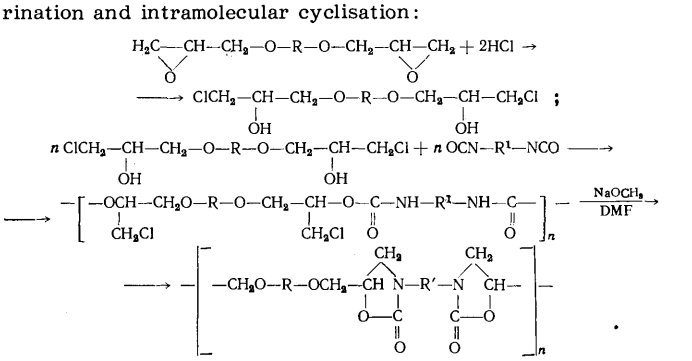
One of the common methods of synthesising poly-2-oxazolidinones involves the reaction of diepoxy-compounds with difunctional urethanes[7,163,175]:



where R = aryl.

It has been shown[175] that the solubilities and melting points of polymers are determined mainly by the structure of the initial diurethane.

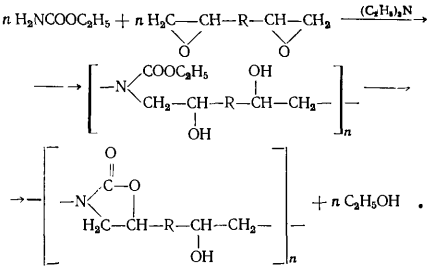
Polyoxazolidinones have been synthesised[176] by the reaction of bischlorohydrins with isocyanates followed by dehydrochlorination and intramolecular cyclisation:



The rate of ring closure depends on the nature of the *N*-substituted polyurethanes. The polyurethanes synthesised from di(4-isocyantophenyl)methane reacts in several

minutes: those obtained from 2,4-tolylene di-isocyanate react more slowly owing to steric hindrance (due to the *o*-methyl group); the cyclisation of the polyurethanes based on tetramethylene di-isocyanate is slower still. The polyoxazolidinones[176] are soluble in DMF and *m*-cresol but are insoluble in acetone, methanol, n-hexane, tetrahydrofuran, dioxan, toluene, and formic acid. The initial polyurethanes with CH_2Cl groups[176] are amorphous substances, while the polyoxazolidinones obtained from them and aromatic di-isocyanates are partly crystalline, and those obtained using aliphatic isocyanates are highly crystalline.

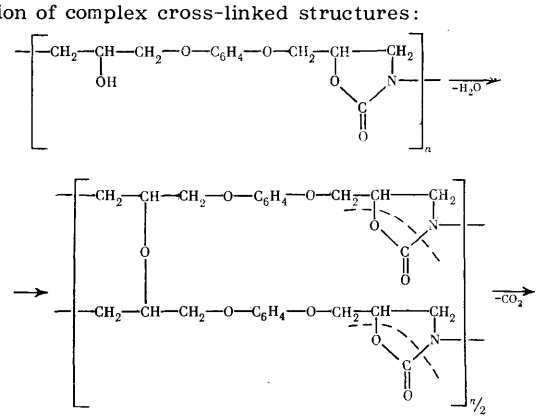
The reaction of ethylurethane with various diepoxy-compounds yielded[177–181] a new class of polymers—linear hydroxylated polyoxazolidinones:

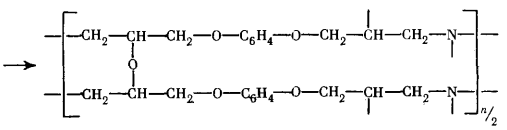


The diglycidyl ethers of hydroquinone, resorcinol, and di(hydroxyphenyl)propane, as well as epoxide oligomers have been used as the diepoxy-component.

The hydroxylated polyoxazolidinones are soluble in the cold in DMF, *m*-cresol, and sulphuric acid. Compared with the usual polyurethanes and hydroxylated *N*-arylpolyurethanes, these polymers have a higher thermal stability, decomposing 260–300 °C above their softening temperatures. The products obtained from the *trans*-forms of the diglycidyl ethers of bisphenols are more resistant to thermal decomposition than the products based on the corresponding *cis*-forms.

The hydroxylated polyoxazolidinones readily react with mono- and di-isocyanates. On oxidation, they give rise to carbonyl compounds, which indicates the presence of secondary hydroxy-groups in their structure. The reactivity of the secondary hydroxy-groups is much higher than that of the second hydroxy-group in isopropyl alcohol, which has been explained[180] by the presence of the oxazolidinone ring nitrogen atom in the β-position relative to them. The hydroxy-groups form intramolecular hydrogen bonds with this atom. The mechanism of the pyrolysis of polymers of this kind has been established by the DTA method in combination with dynamic and isothermal thermogravimetric data[181,182]. It has been observed that the thermal degradation of the oxazolidinone ring is preceded by intermolecular dehydration, which is followed by the decarboxylation of the rings with formation of complex cross-linked structures:



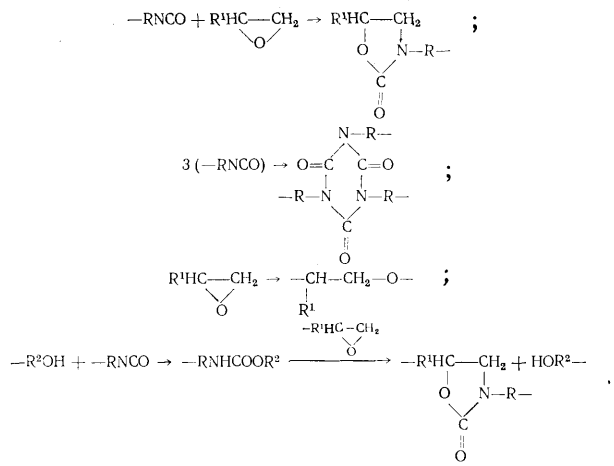


The enhanced reactivity of the hydroxy-groups, the regularity of their arrangement along the polymer chain, and the presence of the thermally stable oxazolidinone rings makes these low-molecular-weight polymers likely to be useful as hardening agents for polyurethane resins[179]. These potential hardening agents can ensure a specified distance between the cross links, which should promote in its turn the reproducibility of properties of the final materials and should improve many mechanical properties. The effectiveness of linear hydroxylated polyoxazolidinones in the hardening of macrodi-isocyanates has been demonstrated[180]. This entails the formation of insoluble and non-swelling very strong polyurethane film materials with good mechanical properties and a higher thermal stability than the polyurethanes hardened by polyols and polyamines.

(b) Cross-Linked Polymers with 2-Oxazolidinone Rings

Several methods of synthesis of cross-linked polymers containing 2-oxazolidinone rings have been described in the Soviet and foreign literature. These are mainly polymers incorporating isocyanurate rings together with 2-oxazolidinone rings.

As already mentioned, the interaction of isocyanates with epoxides involves, apart from the formation of 2-oxazolidinone rings, the competing cyclotrimerisation reaction of the NCO groups. The interaction of epoxide oligomers with di-isocyanates has been investigated[183]. It has been shown that, in the presence of an excess of a di-isocyanate at 160–165 °C, the formation of oxazolidinones is accompanied by the cyclotrimerisation of the isocyanate groups, the homopolymerisation of the epoxy-groups, the reaction of the isocyanates with the compound containing hydroxy-groups, and the reaction between the urethane and the epoxide:



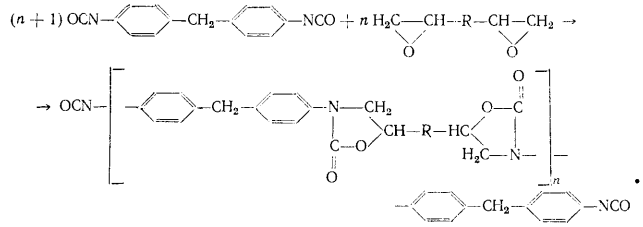
In the synthesis of foam plastics by a single-stage method using an excess of di-isocyanate[60,184] the polymerisation reaction takes place in several minutes and there is virtually no homopolymerisation of the epoxy-groups. The main competing reactions are then cyclotrimerisation and the formation of a urethane.

When tertiary amines are used as catalysts, the epoxide oligomer greatly enhances the catalytic effect in the polycyclotrimerisation of the isocyanate, accelerating thereby this

reaction. The occurrence of competing reactions precludes in this instance the possibility of regulating the distance between the cross links. The considerable brittleness and strain of the foam plastics can be explained by the presence of a large number of isocyanurate rings. The single-stage process takes place[60,184] in the presence of catalysts of the formation of oxazolidinone and cyclotrimerisation, for example, *N,N',N''*-tri[3-(dimethylamino)propyl]hexahydro-*sym*-triazine and the aluminium chloride–hexamethylphosphoramide complex.

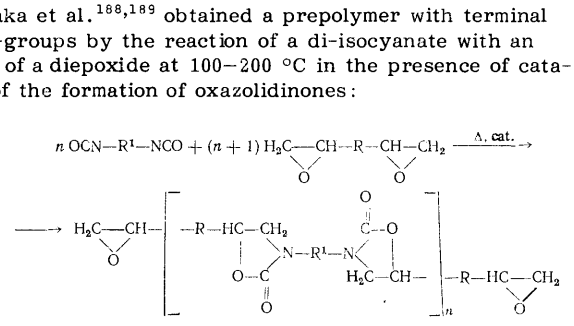
The application of the prepolymer (two-stage) method makes it possible to avoid to a large extent the above difficulties, because cycloaddition (the formation of the oxazolidinone ring) and polytrimerisation (the formation of the polyisocyanurate) take place separately.

Thus the synthesis of an oxazolidinone prepolymer with terminal isocyanate groups has been described[60,185–187]; the synthesis was carried out by the reaction of a diepoxide with an excess of a di-isocyanate at 100–150 °C in the presence of a Friedel–Crafts catalyst ($AlCl_3$, $FeCl_3$, and $ZnCl_2$) for 0.5 to 5 h:



In the second stage the prepolymer is hardened by the polycyclotrimerisation of the terminal isocyanate groups in the presence of catalysts: 2,4,6-tris(dimethylaminomethyl)phenol[185,186] and 2,4,6-tris(dimethylaminoethyl)phenol[60]. However, from our point of view it is doubtful if it is possible to separate clearly and carry out in succession the two reactions—the formation of oxazolidinones and polycyclotrimerisation.

Tanaka et al.[188,189] obtained a prepolymer with terminal epoxy-groups by the reaction of a di-isocyanate with an excess of a diepoxide at 100–200 °C in the presence of catalysts of the formation of oxazolidinones:

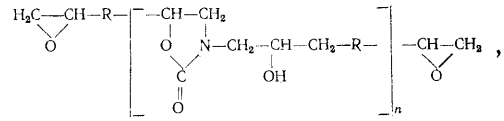


In the second stage an excess of the di-isocyanate was added to the oxazolidinone prepolymer with terminal epoxy-groups and three-dimensional polymers were obtained in the presence of catalysts of the formation of oxazolidinones and polycyclotrimerisation.

Polyisocyanates based on diphenylmethylene di-isocyanate, a mixture of 2,4- and 2,6-tolylene di-isocyanates, and hexamethylene di-isocyanate are usually employed in the synthesis of oxazolidinone-containing polyisocyanurate foam plastics. Among epoxides, applications have been found for epoxide polymers based on 2,2-di(hydroxyphenyl)propane (for example Epon-828 with an epoxide equivalent of 189) and others[60]. Potassium and magnesium ethoxides, aluminium isopropoxide, and iron(III) chloride have been used as catalysts of the formation of oxazolidinones[60].

It has been established[60] that the reaction between unpurified di-isocyanates and the Epon-828 epoxy-resin at 130 °C takes place without the addition of a catalyst. A considerable increase in the viscosity of the reaction medium was observed in the course of the reaction and oxazolidinone rings were formed. However, when purified di-isocyanates were used, a visible increase of viscosity was not observed. The authors[60] explained this by the presence in the unpurified di-isocyanates of admixtures of iron chloride (0.01 wt.%) which catalysed the cycloaddition reaction with formation of oxazolidinone rings.

A method of synthesis of oxazolidinone-containing epoxide oligomers from polyglycidyl ethers of polyols and isocyanuric acid in the presence of catalysts (tertiary amines, quaternary ammonium salts, alkali metal halides and alkoxides, the phosphonium compounds) at 130–180 °C has been described[190]. The reaction takes place with decomposition of the isocyanurate rings and the formation of oxazolidinone rings. The products are oligomers having the general formula



where R is a bivalent residue of the polyglycidyl ether of the polyol and $n = 1–10$. Such oligomers have been synthesised both in bulk and in solvents (DMF, nitrobenzene, *o*-dichlorobenzene, and dioxan). The corresponding derivatives of phenols, bisphenols, Novolak resins, polyoxyalkylene glycols, and aliphatic polyols can be used as the polyglycidyl ethers.

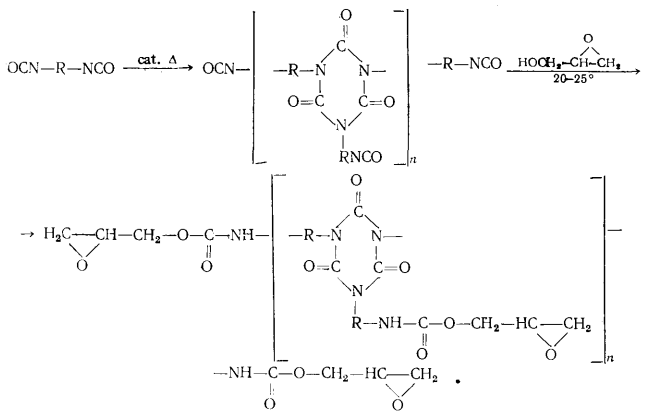
A patent[191] describes the synthesis of thermoreactive resins by the reaction of a polyisocyanate, containing in its structure isocyanurate rings, with a polyepoxide compound, the reaction involving the free isocyanate groups. The resins were hardened at 200–300 °C without a catalyst or at 100 to 185° in the presence of a hardening agent of the amine type.

Oxazolidinone-isocyanurate foam plastics are not very brittle and their combustibility is insignificant. In a study of the influence of the content of the epoxide oligomer in the prepolymer on the physicomechanical properties of oxazolidine-containing foam plastics, it was shown[60,185,186] that an increase of the concentration of the epoxide greatly increases the weight loss in fire tube tests. The content of the epoxide oligomer influences the smoke density particularly when the weight ratio of the epoxide to the isocyanate is greater than 0.1–0.2. An appreciable decrease of the brittleness of the foam plastics is observed when the epoxide : isocyanate weight ratio is approximately 0.05. A further increase of the content of the epoxide entails an insignificant increase of the brittleness[60]. The epoxide : isocyanate ratio (by weight) of 0.05–0.1 may be regarded as optimal.

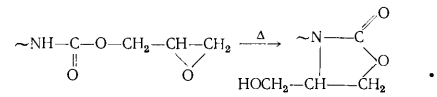
The thermal stability of the foam plastics has been investigated by thermogravimetric analysis (TGA). It was shown[60] that the onset of weight loss is observed at 100 °C and amounts to approximately 30% by 400°. In air, oxazolidinone-isocyanurate foam plastics are more stable than in an atmosphere of nitrogen; in both cases their thermal stability is higher than that of polyurethane foam plastics, evidently owing to the greater stability of the isocyanurate and oxazolidinone rings. It has also been noted[186] that, in contrast to the polyurethane foam plastics and the unmodified polyisocyanurate foam plastics, the mechanical properties of oxazolidinone-isocyanurates are fully isotropic in all directions.

A new method of synthesis of epoxyisocyanurate oligomers has been proposed[92,192–195]. In the presence of polycyclotrimerisation catalysts the initial di-isocyanates were converted into oligoisocyanurates containing isocyanate groups;

then at room temperature the terminal isocyanate groups were made to react with hydroxylated epoxides, for example, with glycidol:



It was shown[192-195] that the hardening of the resulting epoxyisocyanurate oligomers in the presence of hardening agents (acid anhydrides) is accompanied by competing cross-linking reactions involving the epoxy-groups and intramolecular cyclisation with formation of oxazolidinone rings:



However, in the above reports no mention is made of the possibility of the reaction of epoxide rings with isocyanurate rings accompanied by the decomposition of the latter, which has been described in a number of communications[78-80,190].

Hardened epoxyisocyanurates containing 2-oxazolidinone rings have been found to have good physicomechanical properties, to be chemically stable, and to exhibit an effective adhesion in varnish coatings[194]. The temperature of the 10% weight loss by hardened epoxyisocyanurates reached 290 to 300 °C.[88] The ratio of the oxazolidinone rings and cross-links and hence also the physicomechanical and thermal properties can be regulated by the amount of hardening agent and by varying the hardening conditions[88].

3. Applications of Poly-2-Oxazolidinones

Polymers containing oxazolidinone rings are widely used in various branches of modern technology. Their thermal stability and heat resistance are high compared with epoxide materials and polyurethanes and they are more elastic and have more effective physicomechanical properties than polyisocyanurates. By virtue of this set of properties, poly-2-oxazolidinones are used successfully as coatings, varnishes[68,69,156,168,189,190,192,194,196-200], electrically insulating materials[156,188,189,198,201], and binders for various composite materials[156,168,169,190,198,202], in rubber compositions[203], and as adhesives[85,163,168,189,190,197,199], foam plastics[60,68,157-160,184-187,196,204-206], fibres, films[174], corrosion inhibitors[33], etc.[140,144,145,198].

After the manuscript had been sent to the editors, a series of studies on oxazolidinones were published.

Gramain and Remuson[207] described the photochemical oxidation of 2-oxazolidinone which takes place on irradiation by the light of a high-pressure mercury lamp in the presence of O_2 and a 0.1 M solution of Ph_2CO in t-butyl alcohol with formation of oxazolidine-2,4-dione. The study of Itskovich et al.[208] was devoted to the intramolecular cyclisation of diepoxycarbamates with formation of oxazolidinone rings. Kadurina et al.[209] showed that the reactivity of diepoxides in reactions with di-isocyanates decreases in the following sequence: aliphatic diepoxides > aromatic diepoxides > alicyclic diepoxides, the epoxide ring of the alicyclic group altogether failing to react with NCO groups in the absence of a catalyst. According to the authors, steric factors and the lower mobility of the epoxide oligomers with cyclic groups determine their reactivity.

The study of Shukurov et al.[210] was devoted to the synthesis of copolymers of aromatic di-isocyanates and epoxy-resins with high impact strength, hardness, and heat resistance. Sorokin et al.[211] suggest that substituted ureas be used as hardening agents for epoxide oligomers; 2-oxazolidinone rings are then formed in the hardened polymer. Two studies[212,213] were devoted to the synthesis and viscoelastic properties of thermoreactive oxazolidinone-isocyanurate resins. Several patents[214-216] report the synthesis of oxazolidinone-containing polymers. Numata and Kinjo[217] demonstrated the possibility of synthesising oxazolidinone-isocyanurate resins modified by raw rubber. A patent[218] describes the synthesis of 2-oxazolidinone derivatives by the cyclocondensation of substituted β-aminoalcohols with CO_2.

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The Present State of Quantum-chemical Calculations of the Intermolecular Interaction of Polyatomic Molecules

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In the present review, the results of quantum-chemical calculations of the energy of the interaction of polyatomic molecules are discussed for the case of dimers. The main theoretical approaches used in the calculation of intermolecular interaction, the self-consistent field method (supermolecule approximation) and perturbation theory, are analysed briefly. The range of applicability and the advantages and disadvantages of these main approaches are evaluated. The results of non-empirical calculations of the interaction of molecules forming dimers of different kinds: with the participation of hydrogen bonds, donor-acceptor complexes, and others, are examined. The accuracy of non-empirical calculations and the influence of the basis set used are discussed, and recommendations for improving the non-empirical data are given. The possibility of constructing analytical potentials (including atom-atom potentials), which can be used to study many-particle systems, from the results of non-empirical calculations is analysed. In addition to non-empirical calculations, the possibilities provided by semi-empirical methods of calculating the intermolecular interaction of polyatomic molecules both in the self-consistent field approximation and using perturbation theory are also examined. The bibliography contains 202 references.

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I. INTRODUCTION

Intermolecular interactions (IMI) play an important role in many physical and chemical phenomena. The existence of liquid and solid phases, the effects of the self-organisation of biological molecules and more complex structures, solution and adsorption processes, etc. are determined by IMI.

One of the main tasks in the theoretical study of IMI is the study of the potential energy surface for the interaction of two molecules—a dimer. The total intermolecular potential can be obtained from the experimental data only in rare cases, so that extensive use has been made of theoretical approaches to the estimation of IMI using the most varied approximations and methods, from empirical atom-atom potentials to non-empirical (*ab initio*) quantum-chemical calculations. The most reliable data are obtained from precision non-empirical calculations, in which the wavefunctions are constructed using a sufficiently broad set of basis functions (extended basis) and, in addition, account is taken of electron correlation. These calculations are extremely laborious, and up to the present it has been possible to use them to study only the interaction of atoms and various small molecules. To analyse

the IMI of polyatomic molecules, it is necessary to carry out less rigorous non-empirical calculations using restricted basis sets. For complex molecules, however, even these calculations are extremely laborious, and often present an insoluble computational problem, and it is then necessary to resort to the semi-empirical methods of quantum chemistry; the results of non-empirical calculations for model molecules with a small number of atoms can be used to estimate the reliability of semi-empirical methods.

Data on the potential energy surface of the dimer make it possible to proceed to the study of a system of many molecules and to study the structure and properties of liquids and solids. A natural step on going from the dimer to a system consisting of a large number of molecules is the construction of analytical pair potentials of the atom-atom type, carried out on the basis of information on the potential energy surface, obtained non-empirically. The analytical potentials found in this way are used to calculate various characteristics of polyatomic systems; in a number of cases, the Monte Carlo method is used.

Considerable experience of non-empirical calculations of IMI has now accumulated, calculations have been carried out for a large number of dimers with different types of bonding, and definite ideas exist on the most effective methods of calculation and their accuracy and ranges of application. In the present review, the results of non-empirical calculations of IMI, different methods of constructing analytical IMI potentials on the basis of *ab initio* calculations, and the results of IMI calculations obtained by various semi-empirical quantum-chemical methods are discussed. The review deals chiefly with the results of calculations on polyatomic molecules; the large number of papers dealing with the interaction of atoms and diatomic molecules of the type $H...H^+$, $H...H$, $H_2...H_2$, He...He etc. are not examined in the present work.

II. NON-EMPIRICAL METHODS FOR CALCULATING INTERMOLECULAR INTERACTIONS

There are two main approaches to the calculation of the energy of IMI. One is based on the variation principle. This principle is applied in a system consisting of several molecules, which is regarded as a single quantum system—a supermolecule. The energy of the interaction is calculated as the difference between the energy of the ground state of the supermolecule and the total energy of the corresponding isolated molecules. Since the most widespread method for estimating the energy and constructing the wavefunctions of molecules is the method of molecular orbitals (MO), which are determined from the solution of the Hartree–Fock–Roothaan equations, often called self-consistent field (SCF) equations, this approach will subsequently be called the SCF approximation or the supermolecule approximation. In the second approach, the energy of the interaction of the molecules is determined using perturbation theory, whose application requires a knowledge of the wavefunctions and energies of not only the ground states but also the excited states of the isolated molecules.

1. The Method of Molecular Orbitals and the Basis Sets Used in Non-empirical Calculations

Molecular orbitals are usually constructed as linear combinations of atomic orbitals (LCAO) and are determined from the solution of the SCF equations. The principles of SCF theory have been described in detail in many monographs (see, for example, Refs.1–4), so that only those points necessary for the subsequent discussion will be considered here.

The wavefunction of the system is represented in the form of a Slater determinant, constructed from the MO with allowance for the spin properties of the system. This wavefunction with energy E^{SCF} is an approximate solution of the Schrödinger equation corresponding to the ground state. To obtain a better approximation to the solution of the Schrödinger equation, it is necessary to take account of electron correlation. Although the energy of electron correlation E^{cor} makes up only a small fraction of the total energy, allowance for this energy is nevertheless important in the examination of many properties of molecules, The value of E^{cor} is determined either by the method of configurational interaction (CI) or from perturbation theory.

The accuracy of non-empirical calculations of E^{SCF} and E^{cor} depends on the type and number of the basis AO used in the construction of the MO. If Slater orbitals (ϕ_{STO}) are used as AO, completely satisfactory results are obtained if each AO is represented by a linear combination of two ϕ_{STO} (double zeta basis, DZ). A basis set in which there is one ϕ_{STO} for each AO is called a minimum basis set.

In the Slater basis, however, it is difficult to calculate a number of integrals appearing in the SCF equations. In most cases, therefore, non-empirical calculations are carried out with Gaussian orbitals (ϕ_G). Since these functions decrease too rapidly with distance, to obtain results equivalent to those obtained with Slater orbitals, each of the functions ϕ_{STO} is represented in the form of a sum of several functions ϕ_G, leading to an increase in the number of SCF equations. Grouping of some of the functions ϕ_G (contraction) makes it possible to decrease the number of SCF equations. The most widely encountered basis sets, consisting of Gaussian functions, and the methods for contraction are described in Refs.5 and 6.

To find a wavefunction close to the Hartree–Fock limit, basis sets consisting of a large number of functions are required. At the present time, this procedure can be carried out only for small molecules. Calculations for polyatomic systems are usually carried out in restricted basis sets. In particular, extensive use is made of the minimum STO-3G basis set[7], in which there are three ϕ_G for one ϕ_{STO}. The basis set 4-31G,[8] in which the orbitals of the valence shells are divided into two groups, is close to the DZ Slater basis sets. There are also basis sets containing polarisation functions P, describing AO of the d and f type for atoms of the second period (for example, the basis sets 6-31G* and 6-31G**).[9] The selection of the optimum basis set represents one of the most important problems in non-empirical calculations.

2. The SCF Approximation

In SCF methods, the energy of intermolecular interaction is calculated using the equation

$$E_{int}^{SCF} = E_{AB}^{SCF} - E_A^{SCF} - E_B^{SCF} \quad (1)$$

where E_{AB}^{SCF}, E_A^{SCF}, and E_B^{SCF}, represent respectively the Hartree–Fock energies of the supermolecule AB and the isolated non-interacting molecules A and B. Eqn.(1) makes it possible to obtain only an approximate (Hartree–Fock) value of the energy of interaction, and for the further refinement of the energy of interaction it is necessary to take account of correlation corrections: $E_{int} = E_{int}^{SCF} + E_{cor}^{SCF}$. The correlation energy is made up of the intramolecular and intermolecular correlation energies. The most significant for

IMI is allowance for intermolecular correlation, which at large distances is equivalent to the dispersion energy E_{disp},[10] obtained in perturbation theory.

Calculations in the SCF approximation can be divided into three classes, depending on the nature of the basis set used.

1) Calculations in Hartree–Fock basis sets taking complete account of correlation. The accuracy of the results of these calculations is comparable with that of experiment, but the calculations can only be carried out for small systems. Calculations of this kind have been reviewed in Ref.11.

2) Calculations in DZ + P extended basis sets, and also in the basis sets DZ, 6-31G**, etc., are restricted to comparatively small systems, but their range of applicability is expanding rapidly.

3) The most widely encountered calculations are those in restricted basis sets (of the type 4-31 G) and particularly in minimum basis sets. As shown below, calculations in minimum basis sets can be applied to fairly complex systems.

In calculations in extended, restricted, and minimum basis sets, allowance for electron correlation usually reduces to the calculation of the dispersion energy.

The accuracy of calculations in restricted basis sets can be increased if the basis set superposition error (BSSE) is eliminated; this error arises because the basis set in the calculation of the supermolecule AB is broader than that in the calculation of the isolated molecules A and B. To eliminate this error, the calculation of E_A^{SCF} and E_B^{SCF} is carried out in the basis set used for the system AB (the counterpoise (CP) method[11,12].

For the analysis of the physical nature of IMI, it is of considerable interest to separate E_{int}^{SCF} into its components, although this separation is somewhat arbitrary. The principal components of E_{int}^{SCF} are the electrostatic energy ($E_{el\text{-}st}$), the exchange energy (E_{exch}), the induction (or polarisation) energy (E_{ind}), and the energy of delocalisation or charge transfer (E_{ct}), so that it is possible to write:

$$E_{int}^{SCF} = E_{el\text{-}st} + E_{exch} + E_{ind} + E_{ct} \qquad (2)$$

Effective methods exist[13–16] for separating E_{int}^{SCF} into its components. Usually, E_{ct} is determined as the difference $E_{int}^{SCF} - (E_{el\text{-}st} + E_{exch} + E_{ind})$. It is only in the improved scheme proposed in Ref.14 that E_{ct} is calculated directly, and an additional component is introduced, $E_{mix} = E_{int} - (E_{el\text{-}st} + E_{exch} + E_{ind} + E_{ct})$, in which account is taken of interactions of higher orders between different components.

The MO LCAO SCF approximation is now the principal method in non-empirical calculations of IMI for polyatomic molecules, since there exist well developed procedures for solving the Hartree–Fock–Roothaan equations. On the other hand, the procedure for calculating IMI using perturbation theory is still not fully developed (see below). Another advantage of the SCF method is the possibility of studying the interaction of molecules at short distances.

3. The Approximation of Perturbation Theory

In perturbation theory (PT), the Hamiltonian H_{AB} of the system AB is written as follows:

$$H_{AB} = H_A + H_B + V_{AB} = H_0 + V_{AB} \qquad (3)$$

where H_A and H_B are the energy operators of the isolated molecules A and B, V_{AB} the operator of the interaction, regarded as a perturbation, and $H_0 = H_A + H_B$. For large intermolecular distances (0.5–0.8 nm) it is possible to use as the basis functions of perturbation theory the products of the wavefunctions $A_i^0.B_j^0$ of the isolated molecules (i and j are the indices for the states). This method makes it possible to estimate the long-range components of E_{int} : $E_{el\text{-}st}$ in first-order perturbation theory, and E_{ind} and E_{disp} in second-order[11,17–19]. At distances close to the van der Waals minimum (0.3–0.4 nm), it is necessary to take account of exchange effects, and as functions of zeroth order it is necessary to take the antisymmetrised products $\mathscr{A}(A_i^0.B_j^0)$, which, however, unlike the products $A_i^0.B_j^0$ are not eigenfunctions of the Hamiltonian H_0. This leads to difficulties in the construction of the series of perturbation theory.

In the "symmetrical" approaches to this problem, the operator H_{AB} is divided more or less arbitrarily into $H^0 + V^{AB}$ [$H^0 \neq H_0$, $V^{AB} \neq V_{AB}$, compare with Eqn.(3)] in such a way that the antisymmetrised products $\mathscr{A}(A_i^0.B_j^0)$ are eigenfunctions of the operator H^0.[18,20,21] This makes it possible to take account of exchange effects using ordinary perturbation theory. The "non-symmetrical" formalism starts from the natural choice of H_0 and V_{AB} [Eqn.(3)], but in the expansion, forced antisymmetrisation of the wavefunction is carried out by means of the appropriate projection operators. Different "non-symmetrical" perturbation schemes differ from one another in the choice of projection operators and the method of applying them[22–27]. Although the two approaches in principle give equivalent results[18], the "non-symmetrical approaches" have been more widely used.

Different versions of perturbation theory have been used to carry out detailed studies of interaction in the simplest systems (H...H, He...He). The results obtained, in particular the ratio of the contributions of second and third orders, make it possible to state[18,26,28] that in the attraction region the interaction between molecules with closed shells can be explained by restricting the treatment to terms of second order, that is by representing approximately the IMI energy in the form:

$$E_{int}^{PT} = \Delta E^{(1)} + \Delta E^{(2)} \qquad (4)$$

where $\Delta E^{(1)} = E_{el\text{-}st} + E_{exch}$ is the first order contribution, $\Delta E^{(2)} = E_{ind} + E_{disp} + E_{exch}^{(2)}$ the second order contribution, and E_{exch} the second order exchange energy, taking account of the exchange corrections to E_{ind} and E_{disp}. This conclusion is confirmed by calculations for more complex systems[29,30].

The different versions of perturbation theory generally differ only in the expressions for $E_{exch}^{(2)}$.

Precise calculations of the interaction H...H and He...He have shown[18] that the contribution of $E_{exch}^{(2)}$ represents a few percent of E_{int}^{PT}. This contribution has not been estimated for more complex systems, but a precise calculation for the dimer $(H_2O)_2$ showed[30] that satisfactory values of E_{int}^{PT} are obtained without taking account of E_{exch}. It may be assumed that the part played by $E_{exch}^{(2)}$ is also small in the case of the interaction of polyatomic molecules. A rigorous analysis of E_{ind} [28] showed that in the range of non-negligible overlap, allowance for induction interaction requires the introduction of significant ionic terms into the wavefunction. This means that for the correct calculation of E_{ind}^{PT} it is necessary to use as basis functions the wavefunctions of excited states, which contain ionic terms, that is states with charge transfer.

Thus in the calculation of the interaction energy from perturbation theory in extended basis sets which make it possible to take account of ionic states, it is possible to restrict the treatment to the contributions $E_{el\text{-}st}$, E_{exch}, E_{ind}, and E_{disp}. If however the basis set of the excited states is restricted and does not contain ionic terms, it is necessary

to take direct account of the contribution of E_{ct}. This quantity is used in explicit form in the perturbation theory developed by Murrell and co-workers[31], and also in the "symmetrical" theory[20].

The possibilities provided by perturbation theory and the SCF method can now be compared. Unlike E_{int}^{SCF}, the quantity E_{int}^{PT} contains E_{disp} directly. For the other components, for exact (correlated) wavefunctions, the calculation of the electrostatic and exchange energies from perturbation theory and in the SCF approximation leads to identical results. The differences for the Hartree–Fock limit are also negligible. In the calculation in a basis set containing ionic terms, E_{ind}^{PT} corresponds to the sum of E_{ind}^{SCF} and E_{ct}^{SCF} from Eqn.(2) (it must be borne in mind that E_{ind}^{SCF} and E_{ct}^{SCF} also contain added terms from higher order contributions). In the calculation in restricted basis sets without ionic states, E_{ind}^{PT} is compared only with E_{ind}^{SCF},[29] but in this case it is necessary to estimate E_{ct}^{PT}, for example according to Ref. 31. It is suggested[18] that $E_{exch}^{(2)}$ corresponds to a certain fraction of E_{ct}^{SCF}.

There are grounds for assuming that the SCF method and perturbation theory give equivalent results[29,30,32], particularly in calculations in extended basis sets[30]. The methods of perturbation theory have as yet been little tested for polyatomic molecules, and at present, the great majority of non-empirical calculations of IMI for complex molecules are carried out by the SCF method.

The questions dealt with in this section are examined in more detail in monographs[11,17]† and reviews[18,19]. The most complete analysis of "unsymmetrical" perturbation theory is given in Refs. 19, 26, and 27.

III. NON-EMPIRICAL CALCULATIONS FOR DIMERS OF DIFFERENT CHEMICAL CHARACTER

The IMI calculations discussed in this section were carried out chiefly in restricted basis sets. As indicated above, this means that the data obtained in the calculations on the equilibrium geometry and energy of interaction may differ slightly from the experimental results.

1. Hydrogen Bonding

Systems with a hydrogen bond have been studied in detail, both theoretically and experimentally (see published monographs[33–35] and reviews[36,37]). The interest in these systems is due to the fact that they include such materials as water and biopolymers. From the theoretical viewpoint, it is of interest to determine why the hydrogen bond is generally stronger than other types of IMI, and has a definite direction in space.

The water dimer can be considered first. Non-empirical calculations have been carried out for this dimer, which have made it possible to determine the three-dimensional structure and bond energy of the dimer and to distinguish the most important factors determining the stability of the dimer. Calculations for the dimer $(H_2O)_2$ have been carried out in different approximations as far as the use of Hartree–Fock basis sets with allowance for correlation. All non-empirical calculations, irrespective of the choice of basis set, indicate that the most favourable of the three possible structures—linear, crossed, and cyclic (Fig. 1)—is the linear structure with a distance between the oxygen atoms R_{O-O} close to 0.3 nm. This result agrees with the experimental data[38], according to which $R_{O-O} = 0.298$ nm and $\theta = 60°$. The magnitude of the energy of interaction depends on the method of calculation. The results of a detailed calculation for the dimer $(H_2O)_2$ by the SCF method and perturbation theory in a basis set close to the Hartree–Fock set are given in Ref. 30. The calculation using perturbation theory gave the components E_{el-st}, E_{exch}, E_{ind}, and E_{disp}. Since the basis functions used to calculate E_{ind} contained functions of the charge transfer type, E_{ind} in Ref. 30 in fact took account of the contribution of E_{ct}. It is natural to compare the sum $E'_{PT} = E_{el-st} + E_{exch} + E_{ind}$ with the quantity E_{int}^{SCF} calculated in the same basis set. It was found (Table 1) that for distances greater than 0.275 nm, E_{int}^{SCF} is reproduced with a good accuracy by the quantity E'_{PT}. The distance $R_{O-O} = 0.3$ nm corresponds to the minimum values of E_{int}^{SCF} and E'_{PT}: $E_{int}^{SCF} = -16.2$ kJ mole^{-1}, $E'_{PT} = -16.1$ kJ mole^{-1}. According to Ref. 39, the Hartree–Fock limit for E_{int}^{SCF} is 16.3 ± 1.1 kJ mole^{-1}. The fact that the minimum values of E_{int}^{SCF} and E'_{PT} coincide provides evidence that the two approaches to the calculation of IMI, based on SCF theory and on perturbation theory, are equivalent. The discrepancies between E_{int}^{SCF} and E'_{PT} at short distances is attributed to the presence in E_{int}^{SCF} of corrections of higher orders, and various other characteristics of the SCF method[29]. When allowance is made for E_{disp} from perturbation theory (see Table 1), the value of R_{equil} is found to be 0.286 nm, and $E_{int} = E_{int}^{SCF} + E_{disp} = -24.3$ kJ mole^{-1}.[30] The data from Ref. 40, obtained for the dimer $(H_2O)_2$ in an extended basis set with allowance for correlation by CI methods are: $E_{int}^{SCF} = -18.1$ kJ mole^{-1}, $E_{int}^{cor} = -3.6$ kJ mole^{-1}, and $E_{int} = -21.7$ kJ mole^{-1}.

From experimental data it is known that the bond energy in the water dimer lies in the range -16 kJ mole^{-1} to -28 kJ mole^{-1}[11,38,41]. The calculation gives satisfactory values for the bond energies, but the scatter in the experimental data makes it impossible to determine which is the best method for taking account of the correlation correction to E_{int}^{SCF}.

The results of calculations carried out for a linear dimer using perturbation theory in a basis set close to the Hartree–Fock set[30] and by the SCF method in different restricted basis sets with separation of E_{int}^{SCF} into its components[42] are compared in Table 2. The data in Table 2 make it possible to follow the influence of the basis set on the results and to analyse the nature of the bond in the dimer $(H_2O)_2$. It follows from Table 2 that the greatest contribution to the bond energy is made by the electrostatic interaction, and the contributions of E_{ct} and E_{ind} are less significant [$E_{disp} = -6.4$ kJ mole^{-1} (Table 1) is also not decisive]. In the STO-3G basis set, the contribution of E_{el-st} is lowered, and the role of E_{ct} is increased. The calculation in the basis set 4-31G leads to an increase in the bond energy in $(H_2O)_2$ as a result of an excessive value of the electrostatic attraction. More balanced data

† See also I.G.Kaplan, "Vvedenie v Teoriyu Mezhmolekulyarnykh Vzaimodeistvii" (Introduction to the Theory of Intermolecular Interactions), Izd.Nauka, Moscow, 1982.

are obtained in the basis set 6-31G**, which contains polarisation functions, but in this case also the role of E_{ct} is increased. It should be noted that the minimum basis set[43], optimised for calculating IMI, in the case of the linear dimer of water gives $E_{int}^{SCF} = -18.6$ kJ mole^{-1} for $R_{O-O} = 0.3$ nm, which is close to the results of the calculation in the Hartree–Fock basis set[39]. The influence of the basis set on the calculated values of E_{int}^{SCF} will be considered below.

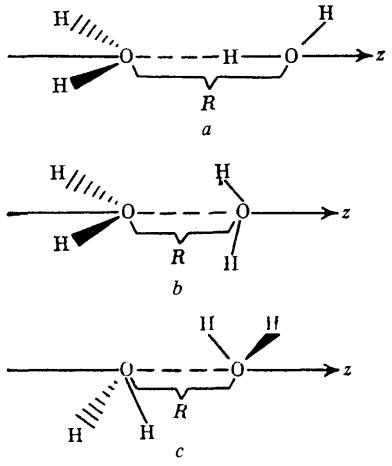


Figure 1. Linear (*a*), crossed (*b*), and cyclic (*c*) configurations of the water dimer[42].

Table 1. Energy characteristics of the IMI, found by the SCF method and from perturbation theory (PT) for the dimer $(H_2O)_2$.

R_{O-O}, nm	E_{PT}	E_{int}^{SCF}	E_{disp}	$E_{int}^{SCF} + E_{disp}$
0.212	54.8	144.9	—60.5	84.4
0.233	13.6	44.9	—35.2	9.7
0.254	—5.3	3.8	—20.5	—16.7
0.275	—13.4	—11.6	—11.9	—23.5
0.300	—16.1	—16.2	—6.4	—22.6
0.370	—12.0	—12.4	—1.3	—13.7
0.476	—4.8	—4.8	—0.2	—5.0

Other examples of small molecules with a hydrogen bond have been examined in a large number of studies. Some of the results obtained in the SCF approximation for different basis sets are given in Table 3 (the data in Table 3 were taken from Ref.43, which gives references to the original papers). The values of E_{int}^{SCF} obtained for $(H_2O)_2$ and $(HF)_2$ in Hartree–Fock basis sets are the most reliable. The bond energies for the systems $HOH...NH_3$ and $H_2O...HNH_2$, calculated in extended basis sets, are slightly too high[43] (absolute values). It may also be noted that a number of calculations carried out without eliminating the superposition error in other basis sets (for example in the standard minimum STO-3G and (7*s*3*p*), denoted OLD in Ref.43, in the minimum basis set NEW, obtained in Ref.43 by optimising the basis set OLD for the calculation of IMI, in the basis set of intermediate type 4-31G, and in the basis set 6-31G*, containing polarisation functions) lead to values of E_{int}^{SCF} which are higher than those obtained using an extended basis set. Elimination of the superposition error by the counterpoise method in the case of calculations carried out in the basis sets OLD and NEW gives results close to those obtained with Hartree–Fock and extended basis sets. Unfortunately, a correct comparison of the values of E_{int}^{SCF} found from the calculation with the experimental data is difficult. Firstly, the experimental data are not always available, and their accuracy is low. Secondly, a meaningful comparison of E_{int}^{SCF} with experiment requires at least an approximate estimate of E_{disp}. Table 3 gives the values of E_{disp} calculated in Ref.43 using an equation of the London type in terms of bond polarisability. Although these values of E_{disp} are too low[44], they nevertheless make up an appreciable part of the total energy of interaction. Allowance for dispersion corrections improves the agreement between the experimental data and the calculated bond energies, obtained by the SCF method in extended Hartree–Fock basis sets and also in the basis sets OLD and NEW. It may be noted that different dimers with a hydrogen bond were also examined in Ref.42 in the basis set 4-31G and without additional allowance for dispersion corrections. The most characteristic properties of hydrogen bonds, which make them unique, were discussed in this paper. The authors[42] studied different dimers, in which the proton donors were HF, H_2O, NH_3, and CH_4, and the proton acceptors HF, H_2O, and NH_3. It was shown that the bond energy E_{int}^{SCF} varies over a fairly wide range from −68.2 kJ mole^{-1} for the complex $H_3N...HF$ to −42.0 kJ mole^{-1} for the complex $H_3N...HF$ to −4.6 kJ mole^{-1} for the $H_2O...H_4C$ system. An analysis of the components of the energy E_{int}^{SCF} found using the published scheme[14] led to the following conclusions about the nature of the hydrogen bond [for the dimer $(H_2O)_2$ see Table 2].

Table 2. Components of the energy of the IMI in the linear dimer $(H_2O)_2$ with $R_{O-O} = 0.3$ nm, obtained in different approximations[30,42].

Components of the energy, kJ mole^{-1}	Perturbation theory[a]	SCF method[b]		
		3-31G**	4-31G	STO-3 G
ΔE[c]	—16.1	—23.4	—32.2	—21.3
$E_{el\text{-}st}$	—29.8	—31.4	—37.2	—17.6
E_{exch}	20.5	18.0	17.6	6.7
E_{ind}	−6.8[d]	—2.1	—2.1	—0.4
E_{ct}	—	—7.2	—8.8	—20.1
E_{mix}^{e}	—	—0.4	—1.7	0.1

[a]Basis set close to the Hartree–Fock set[30]; $R_{O-O} = 0.3$ nm, $\theta = 0°$ (see Fig.1).

[b]$R_{O-O} = 0.298$ nm, $\theta = 60°$. According to Ref.42, the results change little with change in θ.

[c]$\Delta E = E''_{PT}$ in perturbation theory[30] and $\Delta E = E_{int}^{SCF}$ in the calculation by the SCF method.

[d]E_{ind} from perturbation theory contains E_{ct} (see text of the present review and Ref.30).

[e]See discussion of Eqn.(2).

1) All the hydrogen bonds are electrostatic in character, that is the stabilisation is determined chiefly by the electrostatic contribution.

2) The relative part played by E_{ct} is slight in strongly bonded dimers, but increases in weakly bonded dimers.

3) The length and degree of departure from linearity of a hydrogen bond Y–H...X are determined by the ratio of E_{exch} and E_{disp}.

Table 3. Energies E_{int}^{SCF}, kJ mole^{-1}, calculated in different basis sets for the equilibrium configurations of various dimers with a hydrogen bond[43].

Dimer	E_{int}^{SCF}									E_{disp}^{e}	E_{int} (expt)
	OLD[a]	NEW[b]	STO-3G	4-31G	6-31G	OLD (CP)[c]	NEW (CP)	extended basis	HF[d]		
$H_3N\cdots HF$	−59.5	−50.4	−34.7	−68.1	51.0	−49.7	−42.0	—	—	−8.1	—
$HOH\cdots H_3N$	−33.3	−27.8	−24.7	−37.6	−27.2	−25.2	−21.3	−26.3	—	−5.4	—
$H_2O\cdots H_2O$	−31.2	−25.3	−25.1	−33.9	−23.4	−20.4	−18.6	−18.2	−16.3	−3.1	−21.8±6.3
$HF\cdots HF$	−33.1	−22.2	−23.0	−32.2	−24.7	−15.9	−12.2	−19.4[f]	−13.4	−3.6	−25.1±6.3
$H_3N\cdots NH_3$	−15.9	−12.8	−15.9	−17.1	−12.1	−11.1	−9.6	—	—	−2.8	−18.8±1.7
$H_2O\cdots HNH_2$	−15.5	−11.3	−17.1	−17.1	−7.1	−9.2	−8.4	−9.6	—	−2.3	—

[a]Minimum basis set (7*s*3*p*) from Ref.43,

[b]Minimum basis set, obtained in Ref.43 by optimising the basis set OLD for the calculation of intermolecular interaction.

[c]Calculation with elimination of the superposition error by the counterpoise (CP) method.

[d]Hartree–Fock basis set.

[e]Values of E_{disp} calculated in terms of bond polarisability.

[f]See pp.63 and 175 of Ref.11.

Both the calculated and the experimental data indicate that the absolute magnitude of the energy of a normal hydrogen bond does not exceed 60–70 kJ mole^{-1} (ionic hydrogen bonds $NH_3...H^+$ or $FH...F^-$, where the bond energies reach hundreds of kJ mole^{-1}, are not considered here). Comparison of the hydrogen-bonded dimers with the lithium complexes $(LiF)_2$ and $(LiH)_2$ [42] and the strong electron donor–acceptor (EDA) complexes $H_3N...BH_3$ and $BH_3...OC$,[45] in which the bond energy reaches between −150 kJ mole^{-1} and −300 kJ mole^{-1}, makes it possible to estimate the position of dimers with a hydrogen bond in the general series of strongly bonded complexes. The authors[42] consider that the unique character of the hydrogen bond is determined by the fact that in it the proton donor has a short strong bond Y–H of medium polarity. Since the bond has medium polarity, the energy of electrostatic attraction is insufficiently large, and therefore does not compensate the contribution of E_{exch}, which increases rapidly as the atoms H and X approach one another. Since the atoms Y and X are insufficiently far apart, and the bond Y–H is short and its stretching is difficult, the interaction of the atoms Y and X also makes a significant contribution to the exchange energy. In the strong EDA complexes and in the lithium complexes, the strong electrostatic interaction compensates the exchange repulsion, and the atoms of different molecules approach one another to distances less that 0.2 nm [$R_{N...B} = 0.175$ nm in $H_3N...BH_3$, and $R_{Li...F} = 0.180$ nm in $(LiF)_2$]. In the lithium complexes, the bond in the monomer is easily stretched, and this leads to greater possibilities for bond formation in the complex. Thus in $(LiF)_2$ and $(LiH)_2$, the cyclic structure, and not the linear structure, is more favourable. The stretching of the strong bond Y–H, however, requires too great an expenditure of energy. Thus in accordance with published work[42,46], the normal hydrogen bond is characterised by a definite (linear) direction and intermediate energy values.

Various other polyatomic systems with a hydrogen bond can now be considered. A cycle of studies by Pullman and co-workers[47–61] (see also references therein) was devoted to a study of hydrogen bonding involving biological molecules, in particular their mono- and polyhydration. The calculations were carried out in the SCF approximation in restricted basis sets and without additional allowance for E_{disp}. The energy of interaction E_{int}^{SCF} was analysed by the scheme of Ref.15, which is simpler than the schemes of Refs.13 and 14. The contributions E_{el-st}, E_{exch}, and $E_{ind}+E_{ct}$ were separated. The electrostatic energy in some cases was approximated by the energy of interaction of the point multipole moments of the molecules, and this simplifies considerably the estimation of this contribution. Pullman and co-workers have studied in detail the hydration of amides[53,54,57], nucleotide bases[47], urea and thiourea[58,59], and the carboxylate anion[60]; they showed that the characteristic features of the hydration are determined by the magnitude of the contribution E_{el-st}, since E_{exch} and $E_{ind}+E_{ct}$ approximately compensate one another. A more detailed review of this work can be found in Ref.61.

Many authors have studied hydrogen bonding in formamide oligomers[62–66], which provides a model of the interaction in polypeptides and proteins. The most interesting results were obtained for the description of the interaction of amide groups in different configurations, which are characteristic of polypeptides; mention must also be made of the study of cooperative effects[65]. It was recently shown[66] that the attraction of amide groups is stronger in an α-spiral than in a 3_{10} spiral, and cooperative effects were detected on going from the dimer to the trimer.

Table 4. Components of the energy of IMI in the dimers $(HCONH_2)_2$ and $(HCOOH)_2$, calculated in different basis sets (from data in Refs.67 and 68).

Components of the energy, kJ mole^{-1}	$(HCONH_2)_2$	$(HCOOH)_2$		
	STO–3G[a]	STO-3G[a]	minimum basis set	DZ[b]
E_{el-st}	−45.7	−60.0	−94.4[c]	−103.6[c]
E_{exch}	46.5	96.0	89.7	142.9
E_{ind}	−3.2	−3.5	−16.7	−27.5
E_{ct}	−61.2	−97.9	−46.2	−43.1
E_{disp}	—	—	−31.8[d]	−28.0[d]
E_{int}	−63.6	−65.5	−99.6	−59.4

[a]From Ref.67, for $R_{O-O} = 2.73$ Å.

[b]From Ref.68, for $R_{O-O} = 2.7$ Å in minimum and DZ basis sets.

[c]Corrected with allowance for the ratio μ_{calc}/μ_{expt}, where μ is the dipole moment.

[d]Non-empirical calculation using perturbation theory.

The SCF method has been used[67] to study hydrogen bonding in the dimers $(HCOOH)_2$, $(HCONH_2)_2$, and $[B(OH)_3]_2$ in an STO-3G basis set without additional allowance for E_{disp}

(Table 4). The value found for E_{int}^{SCF} (STO-3G) for $(HCOOH)_2$ is close to the experimental value, and amounts to between -60.8 kJ mole^{-1} and -73.3 kJ mole^{-1}.[67,68]. It follows from Table 4 that in the basis set STO-3G, the bond energy in the dimers $(HCONH_2)_2$ and $(HCOOH)_2$ is determined chiefly by the contributions $E_{el\text{-}st}$ and E_{ct}. In the STO-3G basis set, however, the contribution E_{ct} is too large. This follows from a comparison of the components of E_{int}^{SCF} in the dimer $(HCOOH)_2$, obtained in the basis set STO-3G [67] and in the DZ basis set[68] (see Table 4). According to Ref.68, the greatest contribution to the bond energy in $(HCOOH)_2$ is made by $E_{el\text{-}st}$. In the case of the DZ basis set, to obtain results close to the experimental data, it is necessary to take additional account of the dispersion contributions E_{disp}. It may also be noted that the data obtained in Ref.68 were used in Ref.69 to construct model potentials (see R.p. 1073). Calculations carried out in an STO-3G basis set gave satisfactory values for the enthalpies of formation of the dimers of a number of alcohols [70], and were also found to be suitable for the study of the intramolecular hydrogen bond in 7-norbornenol[71]. Mention must also be made of the extensive series of studies by Del Bene (see Refs.72 and 73 and references therein), devoted to the examination of hydrogen bonds in various systems. Lack of space makes it impossible to give a detailed description of the results of recent calculations[74–77] for systems containing a hydrogen bond, such as nitric acid and ammonia, pyrrole and acetonitrile, formaldehyde and hydrogen sulphide, and the sulphide anion and water.

In Ref.78, the $HO^-...H_2O$ system was studied, and data were obtained on the influence of the solvent on the relative acidity of water and methanol.

In most of the work discussed, the MO LCAO SCF approximation was used. Perturbation theory was used in Refs.30, 79, and 80. The last two papers also discuss calculations carried out by the self-consistent field method for the systems $(H_2CO)_2$, $(H_2O)_2$, and $(HF)_2$ in different approximations. Symmetrical perturbation theory[20] has been used successfully [32] to calculate the bond energy in the systems $H_2CO...OH^-$ and $H_2CO...NH_3$.

2. Electronic Donor–Acceptor Complexes

From Mulliken's model for EDA complexes[81] it followed that in these systems an important part is played by charge transfer; in particular, it was suggested that the structure of a complex is determined by the interaction between the occupied MO of the donor and the unoccupied MO of the acceptor. Semi-empirical calculations for EDA complexes[82,83] showed, however, that E_{ct} does not make the decisive contribution to the interaction energy, and the electrostatic interaction is generally more significant. Non-empirical calculations for EDA complexes have begun to appear only comparatively recently. It has been shown[84,85] that in a minimum basis set and the DZ basis, the equilibrium geometries in the complexes formed by H_3N and $(CH_3)_3N$ with F_2, Cl_2, FCl, ClF, SO_2, and O_3 are approximately the same, but higher values are obtained for the bond energy in the DZ basis set. These calculations showed that the bond energy of the complexes of H_3N with F_2, Cl_2, FCl, and SO_2 is greater than the bond energy of the corresponding complexes of trimethylamine. In contrast to the complexes $H_3N...F_2$ and $H_3N...Cl_2$, in the case of the complexes $H_3N...FCl$ and $H_3N...ClF$ the results depend markedly on the choice of basis set. From qualitative considerations, a high bond energy is expected for the complex $H_3N...ClF$, since in the ClF molecule the Cl atom is positively charged, and the N atom in the NH_3 molecule is negatively charged. According to the results of the calculation carried out in the DZ basis set, the bond energy in the complex $H_3N...ClF$ is -32.2 kJ mole^{-1}, and the complex $H_3N...FCl$ is unstable, whereas according to the calculation in the minimum basis set, the complex $H_3N...FCl$ is more favourable. The reason for this lack of agreement between the results of the calculation in different basis sets is apparently that in the minimum basis set it is not possible to estimate correctly the direction of the dipole moment in the ClF molecule.

A systematic study of EDA complexes has been carried out [45,46,86,87]. The calculations were carried out chiefly in the basis set 4-31G. For some of the complexes examined, perturbation theory was used to estimate the value of E_{disp}.

Table 5. Energy characteristics of IMI, kJ mole^{-1}, for the optimised intermolecular distances (R_{equil}), and the classification of the EDA complexes (calculation in the basis set 4-31G).

	Type of complex	R_{equil}	$E_{el\text{-}st}$	E_{exch}	E_{ind}	E_{ct}	E_{mix}	E_{int}^{SCF}	E_{disp}	$E_{int}^{SCF}+E_{disp}$	Classification	Refs.
$H_3N...BH_3$	$n\sigma^*$	0.160	−595.4	570.3	−178.7	−220.5	125.1	−299.2	—	—	s., el-st	[45, 46]
$OC...BH_3$	$\sigma\sigma^*$	0.163	−254.8	413.8	−258.6	−285.8	266.1	−119.6	—	—	s., ct-ind-el-st	[45, 46]
$(CN_2)CO...H_2O$	$n\pi^*$	0.270	−40.6	18.4	−4.2	−7.5[d]		−33.9	−5.0[a]	−38.9	int., el-st	[87]
$(CN)_2CO...H_2O$	$n\pi^*$	0.270[b]	−17.6	8.4	−0.8	−4.6[d]		−14.6[c]	−1.8[a]	−16.2	ditto	[86]
$(CN)_2CO...C_6H_6$	$\pi\pi^*$	0.360	−11.7	7.5	−7.1	−6.7	0.4	−17.6	−10.9	−28.5	int., disp-el-st	[46]
$(CN)_2CO...C_6H_6$	$\pi\pi^*$	0.360[b]	−4.0	2.1	−0.2	−0.6[d]		−2.7[b]	−3.7[a]	−6.4	ditto	[87]
$(CN)_2CO...C_6H_6$	$\pi\pi^*$	0.320[b]	−6.1	12.5	−0.4	−3.1[d]		2.9[b]	−23.3[c]	−20.4		[89]
$Cl_2...C_6H_6$	$\pi\sigma^*$	0.360	−2.1	2.9	−0.4	−3.3	0	−2.9	−2.9[a]	−5.8	w., disp-ct-el-st	[46]

[a] The value of E_{disp} was calculated non-empirically using perturbation theory.

[b] STO-3G basis set.

[c] The value of E_{disp} was calculated in terms of bond polarisability.

[d] $E_{ct}+E_{mix}$.

Breakdown of the energy E_{int}^{SCF} into its components made it possible to determine the interactions responsible for bond formation in the complexes. All the complexes examined were classified according to the values of the bond energy as strong (s.) with E_{int} in hundreds of kJ mole^{-1}, intermediate (int.) with E_{int} in tens of kJ mole^{-1}, or weak (w.) with E_{int} in units of kJ mole^{-1}, and according to the nature of the bond as electrostatic (el-st), induction (ind), and charge-transfer (ct).

The calculated characteristics of some of the complexes examined in these studies are given in Table 5. The data in Table 5 show that the EDA complexes are not charge-transfer complexes. The influence of charge-transfer is different for different EDA complexes and does not correlate with the strength of the complexes. Thus the suggestion[81] that EDA complexes are always charge-transfer complexes was not confirmed in the non-empirical calculations. Significant contributions from E_{ct} were found for the $n\sigma^*$– and $\sigma\sigma^{**}$–complexes formed by polar molecules (H_3N, BF_3, OC, BH_3). These complexes are characterised by strong electrostatic interaction and short equilibrium distances. With decrease in the polarity of the molecules, the complexes become weaker ($H_2CO...F_2$). It may be noted that the values of the energy E_{int}^{SCF} calculated in the 4-31G basis set are found to be too high, since, for example, in the strong complexes $R_3N...BF_3$ and $R_3N...BH_3$ ($R = CH_3$, C_2H_5), which have similar bond character, the experimentally determined values of the bond energy lie in the range from −110 kJ mole^{-1} to −150 kJ mole^{-1}.[88]

Complexes involving molecules containing π-electrons are of considerable interest. For a complex of the type $n\pi^*$ [for example $(CN)_2CO...H_2O$], the most favourable configuration was found to be that in which the water molecule is situated above the plane of the $(CN)_2CO$ molecule[86] (Fig.2). Calculations were carried out in this configuration for the water...tetracyanoethylene (TCE) $n\pi^*$-complex. In these configurations, the stabilisation of the complexes is determined by $E_{el\text{-}st}$.

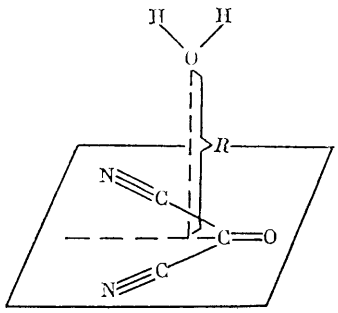


Figure 2. Configuration of the dimer $H_2O...(CN)_2CO$.[86]

The equilibrium distances (0.27–0.30 nm) are greater in the $n\pi^*$-complexes than in the strong $n\sigma^*$-complexes, so that the contributions of E_{ct} and E_{ind} are small. The role of dispersion energy in these systems is slight. It may be noted that the choice of the basis set has a significant influence on the calculated values of the bond energy. For example, in the STO-3G basis set the energy E_{int}^{SCF} of the complex $(CN)_2CO...H_2O$ is −16.3 kJ mole^{-1},[86,87] whereas in the 4-31G basis set it is −38.8 kJ mole^{-1}.[87] The value $E_{int}^{SCF} = -38.9$ kJ mole^{-1} is too high, as is typical of calculations in the 4-31G basis set. The experimental value of the bond energy in the similar system $(CN)_2CO...$diethyl ether is −18.4 kJ mole^{-1}.[86]

For the $\pi\pi^*$-complex $(CN)_2COC_6H_6$ in Ref.87 a "stacking" configuration was chosen, in which the distance between the planes of the molecules and the position of the centre of the benzene ring relative to the C=O axis were optimised (in an STO-3G basis set). A calculation in the 4-31G basis set was carried out for the equilibrium configuration obtained, with $R_{equil} = 0.36$ nm.

The differences in the values of E_{int}^{SCF} for the two basis sets (see Table 5) are due to the characteristic features of the electron distributions obtained in the different basis sets, since these influence the values of $E_{el\text{-}st}$ and E_{ind}. The experimental bond energies for these systems are between −20 kJ mole^{-1} and −25 kJ mole^{-1},[87] which appear to agree only with the results of the calculation in the 4-31G basis set: $E_{int}(4\text{-}31G) = E_{int}^{SCF}(4\text{-}31G) + E_{disp}(4\text{-}31G) = -28.5$ kJ mole^{-1}. It should be noted, however, that the value $E_{disp}(STO\text{-}3G) = -3.7$ kJ mole^{-1}, calculated in the STO-3G basis set using perturbation theory, is clearly too low. The calculation of E_{disp} in terms of the bond polarisability for the dimer $(CN)_2CO...C_6H_6$ being discussed gives the value −13.1 kJ mole^{-1} for $R = 0.36$ nm.[89] Kolos[89] points out that if the more realistic values of E_{disp} calculated in terms of the bond polarisability are added to the values of $E_{int}^{SCF}(STO\text{-}3G)$ from Ref.87, then R_{equil} becomes 0.31 nm, and the bond energy −20.4 kJ mole^{-1} (see Table 5). It may therefore be assumed that the bonding in the dimer involves both dispersion interactions and electrostatic interactions, and the estimate of their contributions to the bond energy depends on the basis set (the value of $E_{el\text{-}st}$ is smaller for the STO-3G basis set, and larger for the 4-31G basis set).

In conclusion, mention may be made of a paper[90] describing a study of charge transfer in the glyoxal-water, $(H_2O)_2$, and $H_2O...Li^+$ systems by different methods (supermolecule, perturbation theory, etc.).

3. Dimers With Other Types of Bond

There have been comparatively few studies of weakly polar or non-polar van der Waals systems, whose stabilisation is determined chiefly by dispersion interactions. Here, mention must be made of detailed studies[91–94] of the potential energy surface for the dimers $(N_2)_2$ and $(C_2H_4)_2$. A significant feature of these studies is that they examined a large number of possible configurations of the dimers and obtained fairly complete information on the potential energy surface.

The authors[91–94] used perturbation theory, and represented the bond energy E_{int} as the sum of $E_{el\text{-}st}$, E_{exch}, E_{ind}, and E_{disp}. The calculations were carried out in DZ and DZ+P basis sets. It was found that in the systems studied, the attraction involves chiefly dispersion interaction; the absolute magnitude of the electrostatic components is several times smaller than that of E_{disp}. The conclusion that E_{disp} plays a decisive role in the stabilisation of dimers containing non-polar systems was also reached by other workers, who calculated the energies of IMI in the dimers $Ar...H_2O$, $Ar...HCl$, $Ar...HF$,[95] and $CH_4...CH_4$.[44] In Ref.44, the results of calculations of E_{int}^{SCF} carried out in different basis sets were given (E_{disp} was estimated in terms of the bond

polarisability), and it was concluded that it is appropriate to use the previously mentioned minimum basis set[43] for IMI calculations. At the same time, as shown by other authors[91,94], although the attraction is determined by E_{disp}, the structure of the equilibrium van der Waals dimers depends to a significant extent on the energy of exchange repulsion E_{exch}. The configurations of the most stable dimers correspond to the lowest exchange repulsion, and in these configurations the attraction (E_{disp}) may not be a maximum. For example, for the dimer $(N_2)_2$ the most stable structure corresponds to the crossed (cross-shaped) arrangement of the molecules[93,94], although the dispersion energy is a maximum in the energetically less favourable linear configuration, in which the exchange repulsion is large. For a distance R between the centres in $(N_2)_2$ equal to 0.4 nm, for the crossed configuration, $E_{exch} = 0.25$ kJ mole^{-1} and $E_{disp} = -1.35$ kJ mole^{-1}, and for the linear configuration $E_{exch} > 3$ kJ mole^{-1} and $E_{disp} = -2.7$ kJ mole^{-1}. The absolute minimum on the potential energy surface corresponds to the crossed structure with values $E_{int} = -1.5$ kJ mole^{-1} and $R = 0.35$ nm.

For the dimer $(C_2H_4)_2$, two structures with low values of E_{exch} were found to be most favourable[92,94]: the staggered parallel configuration and the screw configuration (bond energies -5.01 kJ mole^{-1} and -5.05 kJ mole^{-1} respectively), although the value of E_{disp} is a maximum for the linear arrangement of the molecules, and the value of $E_{el\text{-}st}$ is a maximum for the T-shaped structure. Thus in each case the equilibrium structure of the van der Waals dimer is determined by a fine balance between the forces of repulsion and dispersion attraction, and its determination requires a detailed non-empirical calculation.

These results cast doubt on the reliability of the prediction of the structure of van der Waals dimers on the basis of simple considerations[96,97]. The use of such characteristics of the individual molecules as the dipole and quadrupole moments and polarisability tensors makes it possible to characterise only the long-range contributions of E_{disp} and $E_{el\text{-}st}$, which have been shown to be non-decisive. It has also been suggested that information on the structure of the free dimer can be obtained from the packing of the molecules in the crystal, since the relative arrangement of the nearest neighbours in the crystal should correspond to structures with a low value of the energy of exchange repulsion. The most stable structure of the free dimer, however, may differ from the relative orientation of the nearest neighbours in the crystal. Of the two most favourable structures of the dimer $(C_2H_4)_2$, only one (the screw structure) resembles the packing of the C_2H_4 molecules in the crystal; the staggered parallel structure of $(C_2H_4)_2$, like the crossed configuration of the dimer $(N_2)_2$, differs considerably from the packing of the molecules in the crystal.

Another important result from these studies[92-94] is the conclusion that for the dimers being discussed, there are a large number of structures in which the bond energy amounts to more than 80% of the maximum value. This distinguishes van der Waals dimers from systems with a hydrogen bond and from donor-acceptor complexes, for which there are only a few energetically favourable configurations of the dimers.

Model calculations of the energy of interaction in biological systems are of considerable interest. The study of the interaction of hydroxytryptamines (HT) with the imidazole (IMD) cation has been described in a series of papers[98-100]. The calculation for a system consisting of these fairly large molecules was carried out in a minimum basis set in the "stacking" configuration. Analysis of the components of E_{int}^{SCF} showed that the principal contribution to the stabilisation of the complex is made by electrostatic interaction. The same conclusion was reached in a calculation in a 4-31G basis set with partial allowance for correlation in the interaction of fragments providing models of HT and IMD.[99]

The interactions in the imidazole–methanethiol system, the imidazole–methanethiol–formaldehyde system, and the imidazole–methanethiol–formaldehyde system in the electric field created by the charges on the atoms of an α-spiral which provided a model of the active centre of the enzyme papaine have been studied[101] in minimum and extended basis sets. It was shown that the electrostatic field created by the spiral is responsible for the formation of an ion pair $RS^-...ImH^+$ from the basic residues Cys 25 and His 159. The anomalous values of pK for these residues were also explained[101]. The authors[101] concluded that the α-spirals are important parts of enzymes and play an important role in the catalytic process. An analogous problem and similar substances were studied in Ref.102, where STO-3G and 4-31G basis sets were used to study the interaction in systems containing imidazole, methanol, formic acid, and methanethiol, which provided models of the active centres of serine and cysteine proteases. The number of papers devoted to the non-empirical calculation of the interaction of large molecules is still small, however; the calculation of the interaction of such large molecules as tetracyanoquinodimethane $(CN)_2CC_6H_4C(CN)_2$ and tetrathiofulvene $H_2C_2S_2C_2S_2C_2H_2$ [103] as yet represents the exception.

The thermodynamic stability of dimers at finite temperatures is determined not only by the enthalpy of the system, but also by its entropy. Particular attention was paid to the calculation of the entropy in Refs.104–107. In particular, mention must be made of results[104] which showed that even in polar systems, the role of the entropy term is significant, and in non-polar systems the entropy determines the behaviour of the dimer (see Ref.105). The role of entropy was discussed in Ref.106, devoted to a study of the nature of the stationary points of the potential energy surface for the dimer $(HCl)_2$, and in Ref.107 in a study of the interaction of water with chloroform, fluoroform, and cyclopropane.

IV. NON-EMPIRICAL ANALYTICAL POTENTIALS

The theoretical analysis of IMI for complex many-particle systems is carried out chiefly using simple potentials. The results of non-empirical IMI calculations have recently begun to be used to obtain analytical potentials. An extensive cycle of studies has been carried out by Clementi and co-workers[108-132]. The structure and thermodynamic properties of solutions of ions and biological molecules have been studied. The overall calculation procedure was broken down into three stages.

1. Non-empirical calculations were first carried out for a large number (up to several hundred) different configurations of the corresponding dimer, to obtain sufficiently complete information on the potential energy surface for the system.

2. A set of pair potentials was then chosen in the form of functions of a definite type, depending on the parameters. The parameters were selected to give the best reproduction of the potential surface obtained in the non-empirical calculation.

3. Finally, the analytical potentials obtained in the previous stage were used to calculate the thermodynamic and structural characteristics of the system being studied. Usually, at this stage, the Monte Carlo method was used for the calculation.

The procedure described above was used to study the structure and properties of liquid water[108]. An extended basis set was chosen for the calculation on the $(H_2O)_2$ dimer, and 216 different configurations were calculated in the SCF

approximation. The results of the calculation were approximated by a fairly complex analytical expression consisting of the sum of pair contributions[108].

A calculation by the Monte Carlo method of the radial distribution functions in water and their characteristics gave results close to the experimental data. Particularly good agreement with experiment was obtained using analytical potentials[108] approximating the potential surface of the $(H_2O)_2$ system found with allowance for correlation by the CI method. This result clearly demonstrates the possibilities provided by quantum-chemical methods for estimating various characteristics of many-particle systems.

To investigate the relative role of regular structures in the overall structure of water, the analytical potentials obtained were used to study small regular and non-regular clusters of the form $(H_2O)_n$ ($n = 3$–8). It was found that for the trimer, the most favourable structure is a cyclic structure with symmetry close to C_{3v}; for $n = 4$ and 5, the cyclic structures are energetically most favourable, and for $n = 6$, 7, or 8 there are a large number of non-regular configurations with similar energies. These results, and the fact that the bond energy corresponding to one molecule increases with increase in the number of molecules in the cluster, led the authors[108] to the conclusion that the energy properties of water apparently cannot be described by modelling the liquid phase as an ideal mixture of small regular clusters.

By studying dimers of the type formed by water with the ions Li^+, K^+, F^-, Cl^-, Na^+, etc.[109–112], and also the interaction of water molecules or ions with fragments of proteins and nucleic acids (aminoacids in different forms[113–115], the polypeptide core[116], nucleotide bases[114,117], and phosphate groups[118,119]), Clementi and co-workers created a library of model potentials based chiefly on the results of non-empirical calculations in a minimum basis set. These potentials, and the Monte Carlo method, were used to study a large number of systems. In particular, solutions of ions[120,121] and ion pairs[122,123] in water were examined. Particular attention was paid to the investigation of the structure of water close to nucleotide bases[124], DNA fragments[125,126], aminoacids[127, 128], and various enzymes[129–131]. A detailed analysis of the results of this important cycle of studies is beyond the scope of the present review; they can be found in a recently published monograph by Clementi[132]. It is appropriate, however, to deal with various methodological features of these calculations[108,115].

In the construction of the analytical potentials, Clementi and co-workers took account of the fact that the same atoms in molecules may be present in different valence states (for example, the states of the oxygen atom are different in the OH group, in the C=O bond of the COOH group, and in the C=O group, where the C atom is in an aromatic ring). For most systems (except water), the potentials were chosen in the form of a Lennard-Jones potential with allowance for electrostatic corrections. The reliability of the analytical potentials was estimated from the accuracy of the non-empirical calculations.

In the opinion of the authors of Ref.44, however, the values of the energy E_{int}^{SCF} are determined more accurately in minimum basis sets optimised for the calculation of intermolecular interaction (see for example Ref.43), with elimination of the superposition error by the counterpoise method, than in standard basis sets of the DZ+P type. It is recommended[44, 89] that allowance for correlation be made using perturbation theory, by expressing E_{disp} in terms of bond polarisability, and this has been confirmed by recent results[44].

An analogous series of studies was carried out by Jorgensen and co-workers[133–138]. The calculation procedure was identical to that described above. Systems with hydrogen bonds $(HF)_2$, $(H_2O)_2$, $(CH_3OH)_2$, etc. were studied, and the potentials were taken in the form (12-6-3-1) or (12-6-1). The calculation for the dimer $(HF)_2$ [133,134] was carried out in the 6-31G basis set for 250 points on the potential surface. The model potentials obtained were used to calculate the properties of liquid hydrogen fluoride. The calculations carried out in the 6-31G basis set, however, give a value for the energy of attraction which is too large, so that the calculated heat of volatilisation obtained was too high. Better agreement with experiment was obtained in a calculation for the dimer $(HF)_2$ in the minimum basis set STO-3G. Similarly, in the case of water[136], the results of calculations in the STO-3G basis set also show fairly good agreement with the experimental data. Jorgensen, like Clementi, recommends the use of a minimum basis set in calculations for polar systems, and also that allowance be made for dispersion interactions when non-polar groups are present.

The pair potentials (in the Lennard-Jones form) used in these studies should not be confused with the generally adopted atom–atom potentials, which are capable of reflecting more or less realistically the interaction of individual atoms. Fig.3 gives curves[132] describing the interaction of the oxygen of a water molecule with a nitrogen atom in different fragments of biological molecules. It can be seen that for a nitrogen atom in glycine or asparagine, there is no region of attraction at all. For nitrogen in guanine or 4-hydroxypyridine, however, the potential curves show minima corresponding to equilibrium distances of ~0.30–0.31 nm. The potentials obtained by Clementi and co-workers (Fig.3) and by Jorgensen and co-workers apparently must be regarded only as an analytical approximation to the results of the calculations, making it possible to go from quantities characterising individual molecules to macroscopic quantities, and the physical significance of individual curves cannot be discussed.

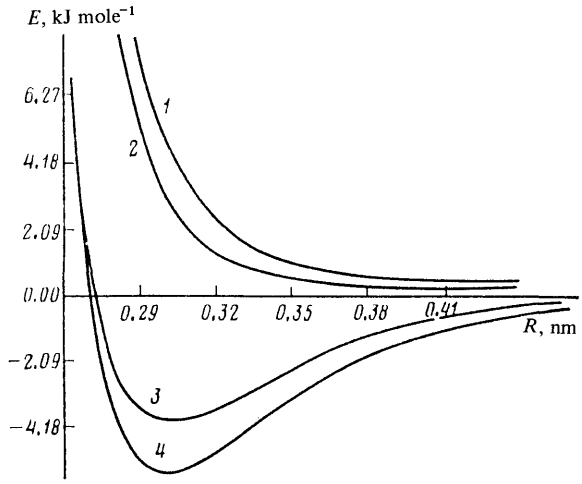


Figure 3. Potentials of the interaction between the oxygen atom of water and a nitrogen atom in different fragments of biological molecules (*1*—glycine, *2*—asparagine, *3*—guanine, *4*—hydroxypyridine).[132]

In another approach, the breakdown of the energy E_{int}^{SCF} into its components is used to construct analytical potentials on the basis of non-empirical calculations. In this case, the

individual components of E_{int}^{SCF} are approximated, and this method makes it possible to reduce the number of configurations whose energy must be calculated non-empirically. Moreover, the pair potentials found in this way acquire a definite physical significance (they can be regarded as non-empirical atom–atom potentials). This method has been used to carry out calculations for crystals of carboxylic acids[68,69]. In Ref.69, the model potentials for the atoms i and j were sought in the form

$$\varphi_{ij} = q_i q_j r_{ij}^{-1} + B^{XY} \exp(-C^{XY} r_{ij}) + A_{XY} r_{ij}^{-6} - D^{XY} \exp(-F r_{ij}) \quad (5)$$

where r_{ij} is the distance between the atoms i and j; q_i and q_j the effective charges on the atoms i and j; and X and Y denote the chemical elements corresponding to the atoms i and j (X, Y = C, O, H).

The individual terms in the right-hand side of Eqn.(5) were compared[69] with the corresponding components of the energy E_{int}^{SCF}, determined in Ref.13, and also with E_{disp} calculated using perturbation theory. The first term in Eqn. (5) was used to approximate the contribution of E_{mult}, where E_{mult} is the part of E_{el-st} which is independent of penetration effects[69]; the second term was used to approximate $E_{ex} + E_{el-st} - E_{mult}$; the third term is compared with the part of $E_{ind} + E_{disp}$ proportional to R^{-6}; and the last term takes account of E_{ct} and the corrections to $E_{ind} + E_{disp}$. The constants A, B, C, D, and F were determined from the results of non-empirical calculations for 12 configurations of $(HCOOH)_2$ and 16 configurations of the dimer $H_2CO...CH_3OP$, which is only one tenth of the number of dimer configurations studied by Clementi and Jorgensen.

The analytical potentials obtained in this way were used[69] to carry out calculations for the dimers of formic and acetic acids and crystals of formic acid and α- and β-acetic acids. The structures found for the dimers and crystals of the carboxylic acids are close to the experimental structures. Unfortunately, the calculation of the energies gives an error of 20–30 kJ mole^{-1} (~30%).

As noted in Ref.69, the errors arising in a calculation of this kind are of different character: for example, they may be associated with the use of restricted basis sets and non-correlated wavefunctions. In addition, errors arise when the analytical potential is fitted to the energy values obtained non-empirically. In Refs.139 and 140, the values of the dispersion energy found in Refs.141 and 142 by a non-empirical method in a DZ basis set for dimers consisting of azabenzenes were approximated as $E_{disp} = \sum_{i \in A} \sum_{j \in B} A_{ij}^{XY} r_{ij}^{-6}$, where r_{ij} is the distance between the atom i of the molecule A and the atom j of the molecule B, and A_{ij}^{XY} represents the parameters of the atom–atom interactions (X, Y = C, N, H). An interesting feature is that the values of these parameters were found to be very close to the empirical atom–atom parameters given by Williams[143]. An attempt to reproduce the non-empirical values of the electrostatic interaction between the azabenzenes in the form of the sum of atom–atom interactions was less successful.

Non-empirical atom–atom potentials have been constructed [92,93] for the dimers $(N_2)_2$ and $(C_2H_4)_2$. Atom–atom potentials have been used[93] to calculate the potential energy surface of the dimer $(N_2)_2$ and various characteristics of the α and β crystalline forms of molecular nitrogen. Analytical atom–atom potentials have been used to carry out a calculation for the ethylene crystal[92].

Non-empirical pair potentials have also been constructed for the complexes formed by water with ammonia[144] and ethanol[145].

V. ACCURACY OF NON-EMPIRICAL CALCULATIONS OF INTERMOLECULAR INTERACTION

Analysis of the above results makes it possible to reach various conclusions about the accuracy of non-empirical calculations. The best agreement with experiment is given by calculations with Hartree–Fock basis sets with complete allowance for correlation (see the calculations of the structural characteristics of water[108]). These calculations, which are close to the exact solution of the Schrödinger equation, can be regarded as standard. These calculations are not readily accessible, however, and it is necessary to know what can be expected from less precise calculations. Here it must be borne in mind that the value of non-empirical IMI calculations lies in their giving not only the quantitative characteristics of IMI but also data on the nature of the bonding in dimers. In addition, the relative values of IMI characteristics may often be useful. The calculation of the correlation energy can be considered first. In the many-configuration approximation, account is taken of both intermolecular and intramolecular correlation. These calculations are much more complex than the calculation of E_{int}^{SCF}, from both the computational and theoretical viewpoints. This is related to the fact that there are serious difficulties in the optimum choice of the excited configurations included in the CI. The treatment is therefore usually restricted to taking account of intermolecular correlation, and E_{disp} is calculated from perturbation theory. To obtain satisfactory values of E_{disp}, it is necessary to use DZ + P basis sets with diffuse polarisation functions P (Ref. 142 and p.60 of Ref.11). DZ basis sets apparently underestimate the value of E_{disp} only slightly, since published data[142] indicate that the DZ and DZ + P basis sets give similar values for E_{disp}.

Calculations carried out in intermediate basis sets, for example in the basis set with split valence 4-31G give values of E_{disp} which are 1.5–2 times smaller than the actual values[87], and minimum basis sets are not suitable for calculating E_{disp}. Kolos and Clementi[44,89] recommend that in these cases E_{disp} should be estimated in terms of the bond polarisability, although the values of E_{disp} obtained are slightly too low[44]. The dispersion energy makes up an appreciable proportion of the bond energy (in the case of van der Waals dimers its role is decisive), but intramolecular correlation may decrease this contribution slightly. For example, the correlation corrections for $(H_2O)_2$ for $R_{O-O} = 0.3$ nm in extended basis sets are −6.4 kJ mole^{-1} (perturbation theory[30]) and −3.6 kJ mole^{-1} (CI [40]). As yet, however, little is known about the influence of intramolecular correlation on E_{int},[146, 18], and this question will not be discussed further in the present review. The correct calculation of the energies E_{el-st} and E_{exch} requires wavefunctions which provide a sufficiently good description of the multipole moments of the molecules. These requirements are satisfied by the wavefunctions found in DZ + P basis sets with polarisation functions P localised close to the nuclei. The correct calculation of E_{ind} requires a DZ + P basis set with diffuse P functions, in which the polarisabilities of the molecules are effectively reproduced. From what has been said above about the basis sets required for the correct calculation of E_{disp}, it is to be expected that non-empirical IMI calculations in DZ + P basis sets with two types of polarisation function should give reliable results. Calculations of this kind are not very practicable for complex systems.

Calculations with DZ basis sets without polarisation functions or with polarisation functions of one type (basis sets 6-31G and 6-31G**, and also the basis sets DZ and DZ + P, described in Refs.92–94) are more readily accessible. The use of these basis sets for the small systems $(H_2O)_2$,[42]

$(HF)_2$,[147] $(N_2)_2$,[93] and $(C_2H_4)_2$ [92,142] has been fairly effective (see Tables 2 and 3). The calculations already mentioned for the crystal of ethylene[92] and molecular nitrogen[93] also indicate that the calculation of E_{int}^{SCF} and E_{disp} in DZ basis sets is reliable from the quantitative viewpoint.

Of the intermediate basis sets, the basis set 4-31G is used most frequently. The energies E_{int}^{SCF} calculated in the 4-31G basis set are apparently more than double the exact values (see the data for $(H_2O)_2$ in Table 2 and the results of the calculation for the dimer $H_3N...BH_3$ in Table 3). The error of the calculation of IMI in the 4-31G basis set is to a large extent related to the overestimation of the electrostatic interaction. Calculations in the 4-31G basis set, however, apparently give sufficiently reliable information on the nature of the bonding in dimers (Tables 2 and 5).

The most widely encountered calculations in minimum basis sets are those for the dimers of polar molecules, particularly dimers with a hydrogen bond. It has been found that in many cases[135-138], E_{int}^{SCF} shows good agreement with the experimental value of the bond energy. This is explained, firstly, by the relatively small contribution of E_{disp} to the energy of the interaction, and, secondly, to the mutual compensation of errors: the energy of repulsion E_{exch} and the electrostatic attraction are underestimated, and the contribution of E_{ct} is overestimated[42]. If however the dimers contain polar and non-polar molecules (for example $(CN)_2CO...C_6H_6$), E_{disp} must be taken into account to obtain the experimental values of the bond energies (see Ref.87 and also Table 5 and R.p.1069). No Hartree-Fock calculations have been carried out for systems of this kind, so that an exact estimate of the accuracy of the calculations in the minimum basis sets is impossible. The STO-3G basis set is apparently unsuitable for calculations for the dimers of non-polar molecules (for example the calculation for $(C_2H_4)_2$ in Ref.91).

The quantitative results obtained in calculations with minimum basis sets must be approached with care, but many other conclusions reached in these calculations (the nature of the stabilising forces, the most favourable structure of the dimer) for the case of polar molecules are also obtained in calculations in broader basis sets.

Kolos, Clementi, and co-workers[43,44] have now pointed out methods for improving considerably calculations in minimum basis sets, based firstly on the elimination of the superposition error and secondly on the use of minimum basis sets specially optimised for the calculation of IMI. This makes it possible to obtain in minimum basis sets results close to those obtained by calculations in extended basis sets not only for polar molecules (Table 3) but also for non-polar systems $[(CH_4)_2]$,[44] if E_{disp} is estimated in terms of bond polarisability.

Thus comparatively reliable results are obtained in calculations in DZ basis sets. It is difficult to reach a final conclusion about the accuracy of calculations in restricted basis sets, but several conclusions can be reached, for example that E_{int}^{SCF} is overestimated in the basis set 4-31G and that satisfactory results are obtained by calculating the interaction of small polar molecules in the basis set STO-3G. It should be noted that authors[86,87,98-100] who have used these basis sets in calculations for large molecules paid particular attention to the qualitative conclusions. The available data indicate that different restricted basis sets give values of the energies E_{int}^{SCF} and their components which differ from one another by a factor of more than two, and it is to be expected that these discrepancies increase with increase in the size of the systems. Thus the absolute and relative differences in the values of the components of E_{int}^{SCF}, calculated in the basis sets STO-3G and 4-31G for the dimers $(CN)_2CO...H_2O$ and $(CN)_2CO...C_6H_6$, increase with increase in the size of the molecules (Table 5), but at the same time the conclusions about the nature of the bond are independent of the basis set.

VI. SEMI-EMPIRICAL IMI CALCULATIONS

Semi-empirical IMI calculations retain their importance in those cases where non-empirical calculations cannot be carried out, for example for a system containing a large number of atoms. Like *ab initio* calculations, semi-empirical calculations are carried out in the supermolecule approximation and using perturbation theory. Supermolecule calculations are most frequently carried out using CNDO, INDO, etc. methods, which are based on neglect of differential overlap (NDO) and use SCF equations. In these calculations, no account is taken of dispersion energy. Unfortunately, the results of most supermolecule calculations carried out in the NDO approximation have proved to be unsatisfactory, and the observed discrepancies when compared with experimental data are not systematic.

Some typical results of IMI calculations in the NDO approximation can be considered. The CNDO/2 method gives a value of the energy of attraction for π-conjugated systems which is much too high. Thus for the $\pi\pi$-complex $C_6H_6...TCE$ in the "stacking" configuration this method gives the values $E_{int} \approx -520$ kJ mole^{-1} and $R_{equil} = 0.175$ nm,[148] whereas experiment gives E_{int} from -7.9 kJ mole^{-1} to -18.1 kJ mole^{-1} and $R_{equil} = 0.33-0.35$ nm.[149] On the other hand, for the dimer $(C_2H_4)_2$ the CNDO/2 calculation gives practically no minimum[150]. For dimers with a hydrogen bond this method often gives satisfactory values of E_{int} and R_{equil}.[151] A calculation by the MINDO/2 method showed that the $\pi\pi$-complex $C_6H_6...TCE$ should not be stable; satisfactory results were obtained for the $n\pi$-complex $NH_3...I_2$, but for the $\pi\sigma$-complex $C_6H_6...I_2$ the energy of attraction was too large[152]. The MINDO/2 and MINDO/3 methods are not suitable for the description of the hydrogen bond[153].

One of the main reasons for the inadequate results of supermolecule calculations in the NDO approximation is the unsatisfactory estimation of exchange terms. In the supermolecule calculation by the CNDO/2 method, account is taken of only the repulsion arising as a result of electrostatic interaction, parameterised in such a way that it leads to repulsion at short distances[154]. Thus for the complex $H_2CO...H_2O$, according to CNDO/2 estimates[13], the energy $E_{int} = -26.3$ kJ mole^{-1}, and from the breakdown of E_{int} into its components according to the scheme in Ref.13 it was found that $E_{el-st} = 20.1$ kJ mole^{-1}, $E_{ind} + E_{ct} = -46.4$ kJ mole^{-1}, and $E_{exch} = 0$. A non-empirical calculation[13] for the same system in the same configuration gives $E_{int} = -14.2$ kJ mole^{-1}, and the contribution of the electrostatic interaction is $E_{el-st} = -19.2$ kJ mole^{-1}; the other values are $E_{ct} + E_{ind} = -23$ kJ mole^{-1} and $E_{exch} = 28$ kJ mole^{-1}. These data show that the values of the individual contributions for E_{int}, obtained from non-empirical calculations, do not agree at all with one another; in particular, the values of E_{el-st} have opposite signs, and E_{exch} in the semi-empirical calculation is equal to zero. The breakdown of the balance between the components of E_{int} in the NDO approximation also leads to the random discrepancies in the results mentioned above. To improve the results, the CNDO/2 parametrisation is modified by changing the values of the intermolecular resonance integrals β. Decrease in β (absolute magnitude) makes it possible to obtain more realistic values of E_{int} for $\pi\pi$-complexes by the CNDO/2 method[155]; at the same time, increase in the value of β led to satisfactory results in a calculation for crystals of small molecules (C_2H_4, N_2, C_2H_2, etc.) by CNDO/2 and INDO methods[150].

In view of these fundamentally unsatisfactory features of the calculations in the NDO approximation, it must be concluded that the use of NDO methods to calculate the quantitative characteristics of supermolecules is not effective. Calculations of this kind may be useful, however, when dimers of similar chemical structure are being compared, and it is sufficient to know only the relative characteristics of the IMI in these dimers. For example, they have been used to determine the preferred configuration of approaching molecules in replacement or addition reactions[156,157] and to compare the qualitative characteristics of complexes with similar structures[158].

Calculation by the extended Hückel method (EHM) usually gives unsatisfactory results. This is related to the fact that in the EHM, account is taken of only the IMI components that depend on the overlap integrals, which at distances equal to or shorter than the van der Waals radius lead to repulsion. In Ref.159, the results of a calculation for the complex $(N_2)_2$ by the EHM were supplemented by calculating the dispersion energy, and in this approximation, good agreement with experiment was obtained for various characteristics of a molecular crystal of N_2. This approach has not been extended further, however. It may also be noted for excimers and exciplexes[160,161].

It is possible to avoid the extensive breakdown of the balance between the components of E_{int}, characteristic of semi-empirical IMI calculations in the supermolecule approximation, if the semi-empirical IMI calculation is carried out using perturbation theory. In the first semi-empirical calculations by purturbation theory, devoted to EDA complexes[82,83,162,163,164], it was assumed that the IMI energy can be represented in the form $E_{int} = E_{exch} + E_{ct} + E_{el\text{-}st} + E_{ind} + E_{disp}$ (that is the results of the theory of Murrell and coworkers[31] were used). Murrell's theory forms the basis of the semi-empirical calculations of IMI using perturbation theory, carried out at the present time. It is possible to distinguish two approaches to the estimation of the components of E_{int}. Studies in which the various components of E_{int} are calculated using the wavefunctions of the isolated molecules, obtained by some single method (usually the CNDO/2 method), can be considered first. In Ref. 154, all the integrals appearing in the expression of the theory[31] were calculated approximately. The differential overlap between AO relating to the same molecule was neglected, and account was taken of the overlap between the AO of different molecules. In Ref.165, to estimate the intermolecular integrals containing differential overlap, the Mulliken approximation was used at the AO level, but in Ref.166 this approximation was applied to the MO. This technique reduces considerably the number of two-electron and one-electron integrals, and simplifies the structure of the expressions under the integral sign. The other integrals are estimated using the approximations characteristic of the CNDO/1 and CNDO/2 methods.

A detailed analysis of possible versions of the approximations was carried out in Ref.154, where it was shown that the application of the Mulliken approximation to the MO gives better results than its application to the AO. In the latter case, the calculated energy E_{exch} is too large. (In Ref.154 it is pointed out that to obtain correct results for the $CH_2...CH_2$ system and for various other systems, the value of E_{exch} must be decreased by a factor of 10 relative to the data in Ref.165!) Ref.154 gives an optimum set of approximations, denoted PE-1 by the present authors. The application of PE-1 to the dimers $(H_2O)_2$ and $C_6H_6...(CN)_2CO$ gives results close to those of non-empirical calculations carried out in an STO-3G basis set (Table 6).

An approximate calculation of all the integrals required for the application of Murrell's theory was also carried out in Ref. 167, where complexes of nucleotide bases with hydrogen bonds were examined. In Refs. 168–170, devoted to an analysis of the interaction of molecules containing silicon, the wavefunctions of the isolated molecules, obtained by the CNDO/2 method, were used for the semi-empirical calculation of all the integrals appearing in "symmetrical" perturbation theory[20]. In the works cited above[154,165–170], the wavefunctions of the isolated molecules were calculated by the CNDO/2 method, after which perturbation theory was used. Perturbation theory is used in a slightly different form in the PCILO method[171,172]. Analysis of IMI by the PCILO method in the CNDO/2 parametrisation gives much better results[173,174] than supermolecule calculations by the CNDO/2 method.

Table 6. Energy characteristics of the IMI, kJ mole^{-1}, for the dimer $C_6H_6...(CN)_2CO$, obtained by different methods.

Method	E_{exch}	E_{ct}	$E_{exch} + E_{ct}$	$E_{el\text{-}st}$	E_{ind}	$E_{int} - E_{disp}$	E_{disp}	E_{int}	Refs.
				$R = 0.30$ nm					
STO-3G	28.7	−6.5	22.2	−8.7	−0.5	13.0	−9.0[a]	4.0	[87]
PE-1	18.5	−7.8	10.7	−4.2	−0.3	6.2	−10.5[b]	−4.19	[154]
PE-2	34.4	−12.0	22.4	−6.3	−1.7	14.4	−27.3[b]	−12.9	[188]
				$R = 0.32$ nm					
STO-3G	12.5	−3.1	9.4	−6.1	−0.4	2.9	−6.6	−3.7	[87]
PE-1	8.7	−3.5	5.2	−2.3	−0.2	2.7	−8.2	−5.5	[154]
PE-2	16.1	−5.7	10.4	−5.5	−1.3	3.6	−20.0	−16.4	[188]
				$R = 0.36$ nm					
STO-3G	2.1	−0.6	1.5	−4.0	−0.2	−2.7	−8.7	−6.4	[87]
PE-1	1.8	−0.7	1.1	−1.1	−0.1	−0.1	−5.3	−5.3	[154]
PE-2	3.3	−1.2	2.1	−5.2	−0.7	−2.8	−11.3	−14.1	[188]

[a] E_{disp} calculated using perturbation theory in a basis set of wavefunctions.

[b] E_{disp} calculated in terms of bond polarisability.

In many calculations, the components of E_{int} are estimated using different approximations, corresponding to the physical nature of the individual contributions. In these calculations, the representation of the components of E_{int} as the sum of terms characterising the interactions between the separate fragments of the molecules (atoms or groups of atoms) is widely used. This approach is based on the possibility of representing the density matrix of the molecule as the sum of local charge densities. In the case of the long-range components $E_{el\text{-}st}$, E_{disp}, and E_{ind}, the potential for the interaction between the local charge distributions can be represented as a multipole series, and it is possible to obtain, for these components, multipole many-centre expansions, which reduce to simplified equations. In particular, the value of $E_{el\text{-}st}$ is usually estimated in terms of the energy of the interaction of atomic multipoles (up to quadrupoles), and in the calculation of E_{disp}, the treatment is restricted to dipole-dipole terms, and E_{disp} is expressed in terms of the bond polarisability tensor and the effective ionisation potentials. The energy E_{ind} is expressed in terms of the bond polarisability and the atomic multipole moments. In the calculation of $E_{el\text{-}st}$ and E_{ind}, the atomic moments are calculated by a semi-empirical method, suitable for these purposes (CNDO/2 or EHM),[175] and the bond polarisability values for the calculation of E_{ind} and E_{disp} are taken from experiment.

An analysis of various simplified expressions for the long-range components is given in various reviews[18,176,177] and other works[178,179].

Simplified equations are also used to calculate E_{exch}. Murrell and co-workers[31] showed that the energy E_{exch} of two one-electron atoms can be approximated successfully by the expression CS^2/R, where S is the overlap integral of the corresponding atomic orbitals. For a polyatomic system, an expression of more general form is used: $\sum_a \sum_b C_{ab}S_{ab}^2/R_{ab}$, where a and b are the atomic orbtials of the interacting molecules. The constants C_{ab} are chosen from a comparison with non-empirical calculations[18,180,181]. Different versions of simplified equations for E_{exch} were discussed in Ref.18.

There are no equations expressing the contribution of E_{ct} to the energy E_{int} as the sum of the interactions between local electron density distributions. This term, therefore, is often not included in calculations using simplified equations [181]; alternatively, it is estimated as $|kS_{mn}*|^2/h\nu_{mn}*$,[83] where $h\nu_{mn}*$ is the energy of the charge-transfer transition, $S_{mn}*$ is the overlap integral of the corresponding MO, and the coefficient k depends on the chemical structure of the interacting molecules[83].

Calculations using simplified equations (or hybrid calculations, as they are sometimes called) have been carried out for different systems. In particular, it has been shown[83,162] that the stability of the EDA complexes C_6H_6...TCE, p-xylene...TCE, and C_6H_6...Hal is determined chiefly by the magnitude of the contributions $E_{el\text{-}st}$ and E_{disp}. These conclusions about the forces bonding the complexes agree with the results of non-empirical calculations (Ref.46, see Tables 5 and 6).

Mention must also be made of a study[162] in which good agreement was obtained between experimental data and the calculated bond energies in complexes of tetracyanoethylene with substituted benzenes. Many studies have been made of the influence of the long-range interactions $E_{el\text{-}st}$, E_{ind}, and E_{disp} between nucleotide bases on the stability of the secondary structure of nucleic acids[179,182]. The long-range components were calculated for two cases, for a hydrogen bond between the nucleotide bases and for their "stacking" configuration. In Ref.183, bond energies for the van der Waals dimers $(N_2)_2$, $(C_2H_4)_2$, and $(C_6H_6)_2$, showing good agreement with the experimental values, were obtained, but the conclusions reached by the authors[183] about the structure of the equilibrium dimers $(N_2)_2$ and $(C_2H_4)_2$ differed from the results of non-empirical calculations[92-94]. This is quite natural, since the non-empirical calculation revealed a large number of structures with energies close to that of the energetically most favourable structure, and the semi-empirical calculation cannot take account of all the fine differences between dimers with similar energies.

In Ref.180 it was shown that the crystal lattice energy of benzene is determined chiefly by two contributions: E_{disp} and E_{exch}. Calibration of the parameters in simplified equations for E_{exch}, E_{disp}, and E_{ind} made it possible[181] to obtain for the dimers of the cations Na^+, K^+, and NH_4^+ with H_2O results equivalent to the results of non-empirical calculations. The use of these parameters made possible a successful description of the interaction of ions with more complex molecules. Various other applications of calculations using simplified schemes have been described[18].

In addition to semi-empirical calculations in which account is taken of all the integrals appearing in the expression for the energy E_{int}, and calculations using simplified equations, there are calculations combining these two approaches. The complex $C_6H_6Cl_2$ has been studied[184]. The contributions E_{ind} and E_{disp} were calculated using simplified equations, and in the estimation of the values of E_{exch} and $E_{el\text{-}st}$, account was taken of all the integrals appearing in the corresponding equations from Ref.31, as was done in Ref.165. As in Ref.165, the value of E_{exch} was found to be much too large. In calculations for the systems $(C_6H_6)_2$, C_6H_6...TCE, naphthalene-TCE,[185] and (pyromellitimide)$_2$,[186] the contributions $E_{el\text{-}st}$, E_{ind}, and E_{disp} were calculated using the simplified equations proposed in Refs.176 and 179, and E_{exch} and E_{ct} were calculated using the MO found by the EHM. These MO in the one-electron approximation were used to calculate the values of the contributions E_{exch} and E_{ct} in accordance with Murrell's theory[31] (this calculation scheme is denoted PE-2). The approach used in Ref.187 to analyse EDA complexes of the $\pi\pi$ type has been justified. The interaction of the π-electrons was taken into account in explicit form, and the interaction of the σ-electron cores was estimated in terms of the atom–atom potentials; the agreement with experiment was satisfactory.

In the analysis of the results of semi-empirical IMI calculations using perturbation theory, it should be noted that a successful choice of approximations makes it possible to obtain useful information on the nature of IMI; the calculated bond enegies and equilibrium distances are often close to the experimental values, and the conclusions about the nature of the forces stabilising the dimers agree with the results of non-empirical calculations.

Table 7. Dependence of E_{int} on the distance R_{O-O} for the dimer $(H_2CO)_2$ in kJ mole^{-1} (data from Ref.189).

R_{O-O}, nm	S configuration[a]		P configuration[a]	
	non-empirical method	PE-2	non-empirical method	PE-2
0.28	—	—	4.1	4.3
0.29	9.5	8.7	1.4	2.0
0.31	1.9	1.6	—0.1	—0.1
0.33	—1.6	—1.5	—1.1	—0.8
0.35	—3.0	—2.7	—1.3	—1.0
0.37	—3.4	—3.0	—	—

[a]For configuration notation see Fig.4.

Table 6 compares the results of calculations for the dimer C_6H_6...$(CN)_2CO$ with allowance for all the integrals (PE-1 approximation[154]) and calculations using the PE-2 hybrid scheme with the results of non-empirical calculations. Although the semi-empirical methods used differ considerably from one another, they give results close to those obtained non-empirically (an exception is the dispersion energy, for which the value obtained in the calculation in a minimum basis set is much too low, irrespective of whether the calculation is non-empirical or semi-empirical).

Calibration of the parameters in semi-empirical schemes to bring their results closer to the results of non-empirical calculations or to experimental data can make it possible to obtain values which are satisfactory from the quantitative viewpoint, and in this case, semi-empirical schemes can be used in the same way as non-empirical pair potentials. Calculations using simplified equations are more suitable for these purposes, since unlike calculations with allowance for all the integrals, these calculations contain parameters convenient for calibration. An example of this approach is provided by the above-mentioned work[181] in which semi-empirical

methods were used to examine the interaction of cations with water molecules and various other molecules. Table 7 gives the results of a calculation[189] for the dimer $(H_2CO)_2$ for the case of antiparallel and perpendicular configurations (Fig.4) in a non-empirical version in Kolos' basis set and by a semi-empirical method using the PE-2 scheme, in which some of the parameters were calibrated from the results of non-empirical calculations. The semi-empirical scheme not only reproduces the difference in the IMI energies in different configurations but also gives results showing quantitative agreement with the results of a non-empirical calculation.

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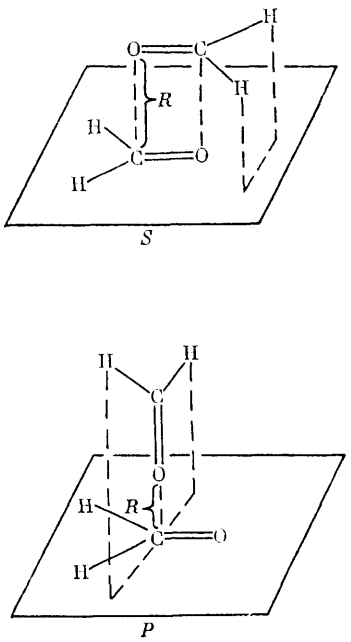


Figure 4. Parallel (*S*) and perpendicular (*P*) configurations of the formaldehyde dimer[189].

Thus the information that can be obtained from IMI calculations depends to a marked extent on the size of the system. If the interacting molecules are small (water, ethylene, etc.) and it is practicable to carry out non-empirical calculations in basis sets of the DZ type, it is possible to obtain satisfactory quantitative results both for a dimer and for many-particle systems.

Non-empirical calculations in restricted and minimum basis sets, which can be carried out for more complex systems, give valuable qualitative results, but their quantitative reliability is low, and appreciable departures from the Hartree–Fock or experimental bond energies (several tens percent) are possible.

Semi-empirical calculations undoubtedly retain their importance in those cases where non-empirical calculations are impossible even in minimum basis sets. Semi-empirical calculations often give results close to the experimental data; with appropriate parameterisation they can be used to obtain results equivalent to *ab initio* data.

The present state of quantum-chemical IMI calculations gives grounds for assuming that IMI calculations will develop in two directions: increase in the accuracy of non-empirical calculations, associated with the development of computational technique, and the creation of flexible semi-empirical schemes making it possible to reproduce experimental and non-empirical data.

While the present review was being prepared for publication, two monographs[190,191] devoted to the analysis of IMI were published. It also seems useful to mention some other recent studies. The influence of the basis set error (BSSE) on the properties of interacting molecules has been examined [192], the breakdown of E_{int}^{SCF} into its components has been analysed[193], and it has been shown[194] for the case of $(HF)_2$ that exchange interactions of second order decrease E_{disp} by 10%. Exchange repulsion has been analysed[195,196]; in particular, SCF calculations of the interaction between valence-non-bonded atoms have been used to obtain simple atom-atom potentials for E_{exch}.[195]

It has been shown non-empirically in a 4-31G basis set[197] that chloroform can bring about the rupture of peptide bonds, and this possibly explains its anaesthetising action. An additive semi-empirical scheme[181] has been used[198,199] to analyse the interaction of biologically active molecules with ions. A semi-empirical IMI calculation scheme which uses an expansion with respect to inverse powers of the intermolecular distance has been proposed[200]. Super-molecule *ab initio* calculations and semi-empirical calculations using perturbation theory have been compared for the case of the hydrogen bond and ion pairs[201]. Various present-day theoretical and experimental problems relating to IMI have been examined in a collection of IMI papers[202].

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The Mechanism of the Decomposition of Organometallic Compounds of Transition Metals and the Role of Intermediate Species in Catalysis

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The three pathways leading to the decomposition of organometallic compounds of transition metals (Mo, W, Ta, Re, Pt, Pd, Rh, Cr, Nd, Y, and Nb) at the instant of formation are examined. α-Decomposition accompanied by the formation of carbene and carbyne species is of decisive importance for methyl, benzyl, trimethylsilylmethyl, and neophyl derivatives. The decomposition proceeds without superposition of radical stages. The mechanism of the chain metathesis of olefins and cycloolefins under the influence of carbene complexes of transition metals is considered. Ideas concerning the chemical nature of the elementary steps in the hydrogenolysis and isomerisation of the carbon skeleton and the dehydrogenation and hydrogenation of hydrocarbons are put forward on the basis of the hypothesis that the primary step in the oxidative addition of hydrocarbons to zerovalent metals involves the formation of organometallic compounds.
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I. INTRODUCTION

Fairly numerous investigations have been carried out on the decomposition of organometallic compounds of transition metals. In early studies of Kondyrev and Fomin[1], published in 1915, it was shown that the products of the decomposition of the organometallic compounds formed on interaction of alkylmagnesium halides with transition metal halides are saturated and unsaturated hydrocarbons corresponding to the alkyl groups of the initial compounds RMgX. These reactions were subsequently studied in greater detail in numerous investigations by Kharasch and many other workers (see, for example, Refs. 2–10).

The decomposition of alkyl derivatives as a rule results in the formation of the corresponding hydrocarbons R + H and R − H (alkane and alkene) and a certain amount of recombination products (R − R). If R = benzyl, phenyl, neopentyl, or other groups without an H atom in the β-position relative to the C–M bond, then the main decomposition product is R − R. When methyl-lithium interacts with halides of a number of metals, the main products are methane and ethane depending on the nature of the metals[5]:

$$CH_3Li \xrightarrow[\text{Ti, Zr, Mn, Cr, La}]{} \text{mainly } CH_4,\quad \xrightarrow[\text{Au, Fe, Ni}]{} \text{mixture of } CH_4 \text{ and } C_2H_6,\quad \xrightarrow[\text{Ag, Cu}]{} \text{mainly } C_2H_6. \qquad (1)$$

The mechanisms of these reactions are considered mainly on the basis of the hypothesis of free-radical stages. The idea of intermediate radical stages in the decomposition are still used by many investigators to account for the mechanism of the formation of the final reaction products, although there is no direct experimental evidence for this. In particular, the "trapping" of these intermediate decomposition products by styrene may be due to the addition to the latter of an organometallic compound of a transition metal. The present author and his co-workers[11–13] were the first to show experimentally that, in the presence of free-radical acceptors, for example, α-methylstyrene, the composition of the products of the reactions of C_2H_5MgBr and C_2H_5Li with $NiCl_2$, $CoCl_2$, and $TiCl_4$ remains unchanged. The reactions involving $NiCl_2$ and $CoCl_2$ lead to the formation of equimolar amounts of ethane and ethylene; in the reaction with $TiCl_4$, a large proportion of ethylene disappears owing to polymerisation. The absence of radical stages has also been noted in the reactions involving the oxidative addition of ethyl bromide to zerovalent cobalt and nickel[14]. The very fact of the formation of equimolar amounts of ethane and ethylene indicates a non-radical nature of the process, since ethyl free radicals readily abstract a hydrogen atom from the solvent. It has been shown that free radical reactions proceed smoothly in those cases where the reduction of M^{n+1} to M^n in the organometallic compound takes place very readily, for example, with conversion of the stable cobalt(III) or manganese(III) complexes into unstable ionic forms[15]:

$$(acac)_3Co + CH_3COOH \rightarrow (CH_3COO)_2Co + CH_3^{\cdot} + CO_2,$$
$$(acac)_3Mn + CH_3COOH \rightarrow (CH_3COO)_2Mn + CH_3^{\cdot} + CO_2. \qquad (2)$$

Homolytic decomposition at the C–M bond, accompanied by the formation of free radicals, is known for compounds characterised by a low energy of this bond. However, in most cases the energies of the carbon–transition metal bond are 30–60 kcal mol^{-1} [16] and the instability of the above compounds at the instant of formation requires a special explanation. Apart from the decomposition pathways leading to the β-disproportionation (R − H and R + H) and recombination (R–R) products, which have been studied in detail, in many cases α-decomposition, accompanied by the formation of carbene and carbyne complexes of transition metals, is the dominant process.

The formation of the carbene complexes of tantalum in the decomposition of $[(CH_3)_3CCH_2]_5Ta$ and $(C_6H_5CH_2)_5Ta$ has been demonstrated[17,18]. The reaction products were respectively $[(CH_3)_3CCH_2]_3Ta{=}CHC(CH_3)_3$ and $(C_6H_5CH_2)_3Ta{=}CHC_6H_5$. The formation of three and more ethane molecules in the decomposition of tetramethyltitanium has been demonstrated[19]. The α-disproportionation of methyl groups, accompanied by the formation of methane, has been demonstrated in relation to the decomposition of $(CD_3)_4Ti$.[20]

Interest in a more detailed study of the α-disproportionation reactions was aroused by the development of ideas concerning the carbene and carbyne nature of the active centres in the metathetical reactions of olefinic and acetylenic hydrocarbons. The stabilisation of carbenes by transition metals tends to drive the reaction towards the formation of carbene species. The carbene stabilisation effect can be illustrated by the work of Fischer[21], who demonstrated the possibility of synthesising stable carbene complexes of transition metals. As a rule, one or two heteroatoms (O, S, and N) are attached to the carbene carbon atom, while different stabilising ligands are attached to the transition metal.

The free carbenes, formed, for example, in the decomposition of diazo-compounds, are extremely reactive and are incapable of causing the development of selective reactions, while the stable Fischer carbene complexes have a low reactivity. The carbene and carbyne complexes arising in the decomposition of organometallic compounds of transition metals at the instant of their formation and occupying an intermediate position between the above species as regards chemical reactivity are of special interest.

Below we present the experimental results of studies in our laboratory of the contributions of the α-decomposition reactions for compounds of different transition metals.

II. THE MECHANISM OF THE DECOMPOSITION OF ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS AT THE INSTANT OF FORMATION. THE RELATIVE CONTRIBUTIONS OF REACTIONS INVOLVING THE α-DISPROPORTIONATION AND RECOMBINATION OF GROUPS

Organometallic compounds of lithium or magnesium containing groups incapable of β-decomposition [CH_3, $C_6H_5CH_2$, $(CH_3)_3SiCH_2$, $C_6H_5C(CH_3)_2CH_2$] have been used as alkylating agents in the reactions with metal halides. The metals investigated (Pt, Pd, Cr, Rh, Mo, Re, W, Ta, Nb, Co) have found extensive applications in the catalytic reactions of hydrocarbons. In recent years some of them (Mo, W, Re, and Ta) in combination with alkylating agents have begun to be used to initiate the chain metathetical reactions of olefins and cyclo-olefins.

Table 1. The composition of the gaseous products of the reaction of CD_3Li with MCl_n.

MCl_n	CD_3Li/MCl_n	Yield, % of CD_3Li			Balance of CD_3 groups, %	$2CD_4+CD_3-CD_4^*$
		CD_4	CD_3-CD_3	$CD_2=CD_2$		
$MoCl_5$	1	60	4.2	3.8	68	124.2
$MoCl_5$	3	70	1.1	0.8	71.9	141.1
WCl_6	1	11	66	0.8	77.8	88
WCl_6	2	20	46	1.5	67.5	86
WCl_6	4	40	35	0.8	75.8	115

*The overall balance of the groups based on Eqn.(3) is presented.

(a) The reaction of CD_3Li with $MoCl_5$ and WCl_6.[22,23] The reaction was carried out in solution in dibutyl ether at 20 °C for 30 min. The yields of the reaction products are given in Table 1.. The products do not contain hydrogen atoms, which indicates the absence of free-radical stages. The main product is CD_4, which is formed solely as a result of the α-disproportionation reaction:

$$(CD_3)_2MX_n \rightarrow CD_4 + CD_2 : MX_n \qquad (3)$$

However, the yield of CD_4, particularly in the reaction involving $MoCl_5$, is much higher than would follow from Eqn. (3), which is confirmed by the overall balance of CD_3 groups. These results can be explained solely by the intensification of the α-decomposition reactions as far as the formation of carbyne and carbide species:

$$\begin{aligned}(CD_3)_3MX_m &\rightarrow 2CD_4 + CD \vdots MX_m\ ,\\ (CD_3)_4MX_y &\rightarrow 3CD_4 + \text{carbides.}\end{aligned} \qquad (4)$$

CD_2H_2, CDH_3, and CH_4 were isolated in proportions of 4 : 3 : 2 in the decomposition of the resulting precipitate with water, which confirms the formation of species of this kind. It is noteworthy that only a few methylene species are evolved in the form of ethylene or remain bound to molybdenum and tungsten. The carbyne formed is apparently mainly consumed in the reaction with the solvent or with other system components. This phenomenon is also characteristic of the other reactions derived below.

(b) The reactions of $(CH_3)_3SiCH_2Li$ and $(CH_3)_3GeCH_2Li$ with various metal chlorides[24–29]. The reaction was carried out in benzene at 20 °C. When tungsten, molybdenum, tantalum, rhenium, and niobium chlorides were used, the process began in solution, while in the case of cobalt, rhodium, platinum, and palladium chlorides the system was heterogeneous. In this case the metal chloride was taken in a tenfold excess relative to the organolithium compound, which ensured the complete consumption of the latter. The interaction of the organolithium compound with the metal halide can proceed via the following main pathways:

$$(CH_3)_3SiCH_2Li + MCl_n \begin{cases} \longrightarrow (CH_3)_3SiCH_2CH_2Si(CH_3)_3\ , & (5a)\\ \longrightarrow (CH_3)_4Si + (CH_3)_3SiCH : MCl_{n-2}\ , & (5b)\\ \longrightarrow (CH_3)_3SiCl + CH_2 : MCl_{n-2}\ . & (5c) \end{cases}$$

The possibility of the occurrence of radical stages is excluded from consideration, since it has been shown[24] that, when the reaction is carried out in perdeuterobenzene, analogous products without deuterium atoms are formed. When the reactions were carried out in trideuterotoluene ($C_6H_5CD_3$), the tetramethylsilane formed also did not contain deuterium. Pathway (5a) is characteristic of the usual decomposition leading to the formation of a recombination product. Pathways (5b) and (5c) lead to the formation of trimethylsilyl and methylene–carbene complexes respectively.

Table 2 presents the experimental results. The overall balance of trimethylsilylmethyl groups was set up on the basis of twice the amount of tetramethylsilane [in conformity with Eqn.(5b) and the number of groups detected in the form of $(CH_3)_3SiCl$ and $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$]. The main pathway in the decomposition of trimethylgermylmethyl and trimethylsilylmethyl derivatives of tungsten, formed for the ratio $RLi/WCl_6 = 0.5–1.0$, is pathway (5c), leading to the formation of methylene species. In the case of tantalum, niobium, and rhodium compounds, the α-disproportionation reaction [pathway (5b)] predominates. The contribution of this reaction is fairly large for platinum and palladium compounds and even for $CoCl_2$, although the main reaction product in these cases is the recombination product R–R. The formation of appreciable amounts of $(CH_3)_3SiCl$ in the reaction of $(CH_3)_3SiCH_2Li$ with $PtCl_4$ is noteworthy.

The results obtained show that the formation of carbene species in the decomposition of organometallic compounds is characteristic also of platinum group metals and not only of transition metals involved in metathetical reactions.

(c) Reactions of benzyl derivatives of magnesium and lithium with MX_n.[30–34] The composition of the products of the interaction of benzylmagnesium chloride in diethyl ether with various metal halides was investigated. Control experiments in perdeuterodiethyl ether showed that, in the reaction with $PdCl_2$, the amount of $C_6H_5CH_2D$ formed does not exceed 5% of the overall amount of toluene produced. Apparently the formation of $C_6H_5CH_2D$ is due to the metallation of diethyl ether by organometallic palladium compounds. When the reaction of benzylmagnesium chloride with $MoCl_5$ is carried out in perdeuterodiethyl ether, $C_6H_5CH_2D$ is not formed.

Table 2. The composition of the products of the interaction of $(CH_3)_3ZCH_2Li$ with MCl_n.

MCl_n	RLi/MCl_n	Yield, % of theoretical			Overall group balance, %	Refs.
		$(CH_3)_4Z$	$(CH_3)_3ZCl$	$(CH_3)_3ZCH_2-CH_2Z(CH_3)_3$		
		Z = Ge				
WCl_6	0.5	11.2	55.4	—	—	[25, 26]
WCl_6	1.0	11.3	43.5	—	—	[25, 26]
WCl_6	2.0	11.2	34.5	—	—	[25, 26]
		Z = Si				
WCl_6	1.0	17.0	31.5	24—26	90.5	[24, 26]
WCl_6	2.0	23.5	23.5	24—26	95.5	[24, 26]
$MoCl_5$	2.0	31.0	10.0	14	86	[27]
$TaCl_5$	0.5	43.0	10.0	traces	96	[27]
$TaCl_5$	1.0	35.0	12.0	11	93	[27]
$ReCl_6$	0.5	7.6	9.5	81	105.7	[29]
$ReCl_5$	1.0	20.0	5.4	55	100.4	[29]
$NbCl_5$	1.0	40.0	6.0	18	104	[29]
$CoCl_2$	0.1	20.0	traces	61	101	[29]
$RhCl_3$	0.1	43.0	traces	16	102	[28]
$PtCl_4$	0.1	16.0	8.0	55	95	—
$PdCl_2$	0.1	17.0	2.0	55	91	[28]

The interaction of $C_6H_5CH_2MgCl$ with metal halides can proceed via the following principal pathways:

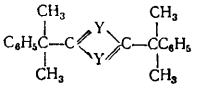
$$C_6H_5CH_2MgCl + MX_n \begin{cases} \longrightarrow C_6H_5CH_2CH_2C_6H_5\,, & (6a) \\ \longrightarrow C_6H_5CH_3 + C_6H_5CH : MX_{n-2} \rightarrow C_6H_5HC{=}CHC_6H_5\,, & (6b) \\ \longrightarrow 2C_6H_5CH_3 + C_6H_5C : MX_{n-3} \rightarrow C_6H_5C{\equiv}CC_6H_5\,. & (6c) \end{cases}$$

The carbene and carbyne fragments can be partly disposed of in the form of stilbene and toluene. The data in Table 3 show that in the reactions of organomagnesium compounds the main product is toluene, in the formation of which 40 to 70% of the benzyl groups of the organometallic compound are consumed. In the reaction with $PtCl_4$ a considerable amount (9–10%) of stilbene is formed.

Particular mention should be made of the fact that in the reactions with $NdCl_3$ and YCl_3 a stable organometallic compound soluble in hydrocarbons is formed in a yield exceeding 90%, to which the following dimeric structure has been attributed:

$$(C_6H_5CH_2)_3Nd\,(Y) \rightarrow 1.8\,C_6H_5CH_3 + 0.5\,C_6H_5C\begin{matrix}\diagup\!\!\diagup Nd\,(Y)\\ \diagdown\!\!\diagdown Nd\,(Y)\end{matrix}CC_6H_5 + \\ + 0.2\,(C_6H_5HC{=}CHC_6H_5 + C_6H_5C{\equiv}CC_6H_5)\,. \qquad (7)$$

In these compounds one fragment of the benzyl group corresponds to each Nd or Y atom. When they are treated with D_2O, $C_6H_5CD_3$ is formed quantitatively. In the reaction with neophenyl-lithium the compound



is formed quantitatively and its hydrolysis yields two t-butylbenzene molecules. In terms of their thermal stability, the complexes produced are analogous to the Fischer carbene complexes.

Table 3. The composition of the products of the interaction of organolithium and organomagnesium compounds (A) with MCl_n in diethyl ether at 20 °C.

MCl_n	A/MCl_n	Yield, % of theoretical				Refs.
		toluene	stilbene	tolane	bibenzyl	
		A = $C_6H_5CH_2MgCl$				
$MoCl_5$	3.0	14—16	0.8—1.5	0.3—0.7	25—27	[30]
WCl_6	0.7	22	0.1	0	7.7	[31]
WCl_6	4.0	17.7	0.5	0	19.1	[31]
$ReCl_5$	3.0	22—27	1.7—2.0	0	18—20	[31]
$RnCl_3$	2.8	26—29	1.2—1.6	0	29—33	[32]
$PdCl_2$	1.5	30—34	0.8—1.2	0	20—38	[32]
$PtCl_4$	4.0	33—34	9—10	0	14—18	[32]
$CrCl_3$	2.5	32—36	1.1—1.4	0	13.8—14.3	[32]
		A = $C_6H_5CH_2Li$				
$NdCl_3$*	2.0	33—57	1.8	0.8	4.2	[33, 34]
YCl_3*	3.0	46	5.0	7.5	4.0	[33, 34]

*In tetrahydrofuran.

Table 4. The composition of the products of the interaction of organolithium and organomagnesium compounds (A) with transition metal chlorides at room temperature.

MCl_n	A/MCl_n	Contribution of reaction, %	
		α-decomposition	recombination (R–R)
	A = CD_3Li		
$MoCl_5$	1—3	96—99	1—4
WCl_6	1—4	34—65	35—66
	A = $(CH_3)_3GeCH_2Li$		
WCl_6	0.5—2.0	46—67	—
	A = $(CH_3)_3SiCH_2Li$		
WCl_6	1—2	74—76	24—26
$MoCl_5$	2	86	14
$TaCl_5$	0.5—1.0	100	0
$ReCl_5$	0.5—1.0	19—45	55—81
$NbCl_5$	0.5—1.0	82—85	15—18
$CoCl_2$	0.1	39	61
$RhCl_3$	0.1	86	14
$PtCl_4$	0.1	45	55
$PdCl_2$	0.1	45	55
	A = $C_6H_5CH_2MgCl$		
$MoCl_5$	3	73—75	25—27
WCl_6	0.7—4.0	81—92	8—19
$ReCl_5$	3	80—82	18—20
$RhCl_3$	2.8	67—71	29—33
$PdCl_2$	1.5	62—71	29—38
$PtCl_4$	4	82—86	14—18
$CrCl_3$	2.5	86	14
	A = $C_6H_5CH_2Li$		
$NdCl_3$	2—3	96	4
YCl_3	3	96	4
	A = $C_6H_5C(CH_3)_2CH_2Li$		
YCl_3	3	100	0

When the reaction of $(CH_3)_3SiCH_2Li$ with $NdCl_3$ was carried out in bromine, stable products were obtained[35] to which the structure

$$(CH_3)_3SiHC{=}Nd{-}CHSi(CH_3)_3\,.\\ \quad\quad\quad\

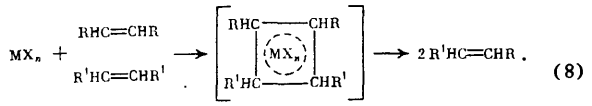
was attributed. When this compound is decomposed with deuterated water, $(CH_3)_3SiCHD_2$ is produced quantitatively.

Particular mention should be made of the considerable contribution of the α-decomposition reaction in the presence of platinum, palladium, and chromium, which are widely used in the catalysis of the reactions of hydrocarbons. Table 4 summarises data characterising the contribution of the α-decomposition reactions leading to carbene species and the contribution of the group recombination reactions (the formation of R–R). It lists the minimum and maximum yields of products obtained for different proportions of organolithium (organomagnesium) compounds and transition metal chlorides.

Thus the α-disproportionation of groups leading to the formation of carbene and carbyne species is in many instances the main pathway in the decomposition of the organometallic compounds of transition metals when the latter do not have hydrogen atoms at the β-carbon atom. As mentioned above, the carbene and carbyne species formed apparently disappear mainly as a result of the reaction with the solvent and only a small proportion are detected as recombination products ($D_2C{=}CD_2$, $C_6H_5HC{=}CHC_6H_5$, and $C_6H_5C{\equiv}CC_6H_5$) and bound as complexes with the transition metal. It will be shown below that the decomposition of the alkyl derivatives of certain transition metals can involve some α-decomposition as well as the main β-decomposition reaction.

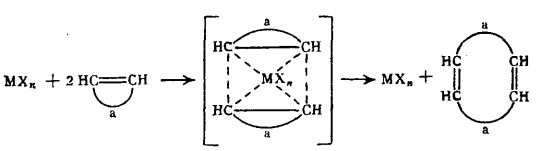
III. THE CHAIN METATHETICAL PROCESS UNDER THE INFLUENCE OF CARBENE COMPLEXES OF TRANSITION METALS

The metathesis of olefins under the influence of molybdenum and tungsten compounds on alumina was first observed by Banks and Bailey[36]. Subsequently systems based on molybdenum, tungsten, and rhenium compounds in combination with organometallic compounds of aluminium, tin, etc. were used widely for these reactions. In their composition, they resemble the Ziegler systems used for the polymerisation of olefins and dienes. The metathetical reactions of olefins in homogeneous systems proceed at the usual temperatures at a very high rate without heat changes. The mechanism proposed initially for this unusual reaction provided for a stepwise process via intermediate stages with formation of quasi-cyclobutane rings having four equivalent carbon atoms[37]:



(8)

Simultaneously and independently Natta and co-workers[38,39] developed their research into the opening of cyclo-olefins under the influence of the same catalytic systems. They showed that the metathesis catalysts initiate the polymerisation of cyclo-olefins at the usual temperatures with formation of polymers in which the double bonds are retained quantitatively. The hypothesis of the intermediate formation of a quasi-cyclobutane ring was used[40] to explain the mechanism of the opening of cyclo-olefins:



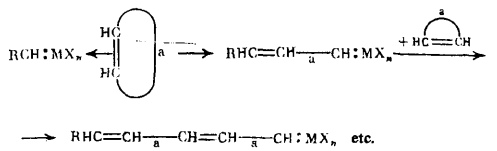
(9)

Calderon et al.[41] were the first to demonstrate that the metathesis of olefins proceeds via a C=C bond dissociation reaction:

$$CD_3DC{=}CDCD_3 + CH_3HC{=}CHCH_3 \rightarrow 2\,CD_3DC{=}CHCH_3\,. \qquad (10)$$

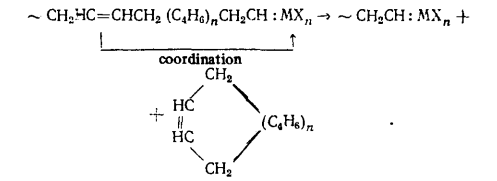
It has been shown in studies[42,43] of the composition of products of the decomposition of the ozonides of a copolymer of a ^{14}C-labelled cyclopentene with cyclo-octene that the polymerisation of cyclo-olefins also takes place with dissociation of the double bonds.

The present author and his co-workers[44–46] showed for the first time that the polymerisation of various cyclo-olefins under the influence of metathesis catalysts results in the formation of high-molecular-weight products at low conversions, oligomers being absent, which constituted direct confirmation of the chain mechanism of the process. The polymerisation of cyclo-olefins initiated by diazo-compounds, which decompose under the influence of WCl_n, was the first experimental evidence for the carbene nature of the active centres[47,48]. The following mechanism of chain propagation under the influence of carbene complexes of transition metals was proposed:



(11)

The polymerisation process consists of consecutive stages in which the monomer is coordinated to the active centre (the carbene complex of the transition metal) and is incorporated in the chain with regeneration of the active centre. The formation of high-molecular-weight products indicated a small number of effective active centres and their comparatively long lifetime. It was shown that unsaturated polymers are readily destructured in solution via the same mechanism with formation of a set of cyclic oligomeric molecules[49–53]:

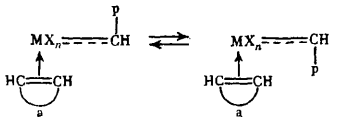


(12)

Thus, high-molecular-weight polybutadiene (molecular weight 200 000) is converted into cyclic oligomers with a number-average molecular weight of 1600 in solution (concentration of raw rubber 8–10%) under the influence of metathesis catalysts after 15 min at room temperature. In the R_2AlCl–$MoCl_3(OCOC_{17}H_{35})_2$ system the oligomers formed retain the *cis*-configuration of the units[53], while in the R_2AlCl–WCl_6 system the ratio of the *cis*- and *trans*-units in the oligomers corresponds approximately to equilibrium. The initial stage of the polymerisation of cyclo-olefins involves the formation of a polymer with a narrow molecular-weight distribution (MWD),[54] which corresponds to a process via a live chain mechanism. The contribution of intramolecular reactions [Eqn.(12)] increases with the degree of polymerisation, which leads to a gradual widening of the MWD.

The $(CH_2{=}CHCH_2)_4Si$–WCl_6 system has been used for the polymerisation of cyclopentene. At −30 °C it gives rise to a polymer containing 98% of *cis*-units, while at +30 °C the product is a polypentenamer with a predominant (~80%) *trans*-configuration of the units[55]. The formation of units with the *cis*- and *trans*-configurations in metathetical reactions is

apparently associated with the rotation of the carbene about the C=M bond:



(13)

where p is the polymer chain.

The energy of rotation of carbenes in the complex $(C_6H_5CH_2)_3Ta{=}X$, where X represents carbene species, has been estimated[56] as 15–22 kcal mol^{-1}. For metathesis catalysts, it is apparently significantly lower and depends on the nature of the transition metal and the ligands surrounding it. The hypothesis of the possibility of such an isomerisation mechanism was first put forward by Ivin et al.[57]

As in other radical anionic chain processes, the metathetical reaction is inhibited by impurities leading to the formation of more stable carbene complexes than those of the growing chain. It has been shown[58–60] that ethyl vinyl ether, butyl vinyl sulphide, and trimethylvinylsilane fully inhibit the cyclopentene ring opening reaction even when present in an amount corresponding to two moles per mole of tungsten:

$$\begin{gathered}
\mathrm{pHC:MX_n + H_2C{=}CHSi(CH_3)_3 \xrightarrow{(a)} pHC{=}CH_2 +} \\
\mathrm{+ (CH_3)_3SiHC:MX_n \xrightarrow{(b)} p'HC:MX_n\ ,} \\
\mathrm{pHC:MX_n + H_2C{=}CHOR \xrightarrow{(a)} pHC{=}CH_2 +} \\
\mathrm{+ ROHC:MX_n \xrightarrow{(b)} p'HC:MX_n\ ;} \\
\mathrm{pHC:MX_n + H_2C{=}CHSR \xrightarrow{(a)} pHC{=}CH_2 + RSHC:MX_n \xrightarrow{(b)} p'HC:MX_n\ .}
\end{gathered} \tag{14}$$

The reaction is inhibited in stages (14b) involving the transition from the relatively stable complex to the more reactive complex formed after the incorporation of the monomer.

It has been shown[51] that in the cometathesis of α-olefins the reaction proceeds preferentially towards the exchange of methylene fragments [degenerate metathesis—reaction (15a)]:

$$\mathrm{R'HC{=}CH_2 + RHC{=}CD_2} \begin{cases} \longrightarrow \mathrm{RHC{=}CH_2 + R'HC{=}CD_2}\ ; & (15a) \\ \longrightarrow \mathrm{R'HC{=}CHR + H_2C{=}CD_2}\ . & (15b) \end{cases}$$

The rate of reaction (15a) is higher by a factor of 10^2–10^3 than that of reaction (15b). The mechanism of this phenomenon was examined and confirmed by the present author and his co-workers[62]. Reaction (15b) can proceed via intermediate stages involving the formation of secondary and primary carbene complexes differing in reactivity:

$$\underline{\mathrm{R'HC:MX_n}} \underset{\mathrm{R'HC:MX_n}}{\overset{\mathrm{H_2C:MX_n}}{\rightleftarrows}} \underline{\mathrm{RHC:MX_n}} \underset{\mathrm{RHC:MX_n}}{\overset{\mathrm{H_2C:MX_n}}{\rightleftarrows}} \underline{\mathrm{R'HC:MX_n}}\ \text{etc.} \tag{16}$$

Under the conditions of the chain process, even small differences between the reactivities of the primary and secondary carbenes cause a marked retardation of the reaction. Reaction (15a) proceeds via a stage in which secondary carbene complexes with identical reactivities are formed:

$$\mathrm{R'HC:MX_n \longrightarrow RHC:MX_n \longrightarrow R'HC:MX_n \longrightarrow RHC:MX_n}\ \text{etc.} \tag{17}$$

Therefore its rate is much higher than that of reaction (15b).

This mechanism has been confirmed experimentally by the results obtained in the cometathesis of β-butene with α-pentene in equimolar amounts under the influence of the R_2AlCl–WCl_6 system at 20 °C. The following reactions can take place in the initial stage:

$$\mathrm{C_3H_7HC{=}CH_2 + CH_3HC{=}CHCH_3 \rightarrow C_3H_7HC{=}CHCH_3 + CH_3HC{=}CH_2}\ ; \tag{18a}$$

$$\mathrm{2\,C_3H_7HC{=}CH_2 \rightarrow C_3H_7HC{=}CHC_3H_7 + H_2C{=}CH_2}\ . \tag{18b}$$

Reaction (18a) should proceed via consecutive stages involving the formation of the carbene complexes $CH_3CH_2.CH_2HC:MX_n$ and $CH_3HC:MX_n$, while reaction (18b), accompanied by the formation of ethylene, proceeds via stages in which $C_3H_7CH:MX_n$ and $CH_2:MX_n$ are formed. It has been established experimentally that the initial reaction product is only propene and not ethylene.

In the first section of this review, pathways leading to the formation of carbene species in the decomposition of organometallic compounds of transition metals capable of β-disproportionation were considered. In metathesis systems alkyl derivatives of aluminium (tin) are used in which there is a possibility of the α- and β-disproportionation of groups. It appeared important to explain the relatively small contribution in the above systems of α-decomposition reactions leading to the formation of carbene active centres. For this purpose, a study was made of the composition of the products formed in the reaction of $(C_2H_5)_2AlCl$ with $MoCl_3(OCOC_{17}H_{35})_2$ and of $C_2H_5AlCl_2$ with $WCl_4(OR)_2$ in the presence of trimethylvinylsilane[58,63]:

$$\mathrm{C_2H_5Mo\,(W)\,X_n} \begin{cases} \longrightarrow \mathrm{C_2H_4 + C_2H_6}\ ; & (19a) \\ \longrightarrow \mathrm{C_2H_6 + CH_3HC{:}\,Mo\,(W)\,X_n}\ . & (19b) \end{cases}$$

In the presence of trimethylvinylsilane, the reaction leading to the formation of the more stable trimethylsilylcarbene species and propene should take place:

$$\mathrm{CH_3HC:MX_n + H_2C{=}CHSi(CH_3)_3 \rightarrow (CH_3)_3SiHC:MX_n + C_3H_6}\ . \tag{20}$$

It has been shown that 3(10)% of propene relative to molybdenum (tungsten) is formed in the reaction. Hence it follows that reaction (19b) plays an appreciable role in the systems considered.

It was noted above that the $(H_2C{=}CHCH_2)_4Si + WCl_6$ system is used for the polymerisation of cyclopentene at −30 °C. It has been shown[64] that the reaction of $H_2C{=}CHCH_2SI(CH_3)_3$ with WCl_6 at room temperature in the absence of the monomer is rapidly completed by the formation of propene in an amount significantly exceeding that permitted by the equation

$$\mathrm{(H_2C{=}CHCH_2)_2WX_n \rightarrow C_3H_6 + H_2C{=}CHCH{:}\,WX_n}\ . \tag{21}$$

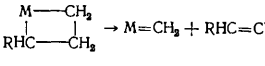
Hence it follows that the reaction of WCl_6 with $H_2C{=}CHCH_2.Si(CH_3)_3$ as well as CD_3Li is more far reaching and involves the formation of the carbyne species $H_2C{=}CHC{\vdots}WX_m$.

A series of studies describing the reactions involving the redistribution of acetylenic hydrocarbons under the influence of carbyne complexes of transition metals have been published recently[65,66]. It has been shown[67] that in the metathesis of acetylenic hydrocarbons under the influence of $(CH_3)_3CC{\equiv}W[OC(CH_3)_3]_3$ the equilibrium composition of product is attained after only 2 min at room temperature:

$$\mathrm{2R'C{\equiv}CR \rightleftarrows RC{\equiv}CR + R'C{\equiv}CR'}\ , \tag{22}$$

where R and R′ = C_2H_5 or C_3H_7.

The metathetical reaction is initiated by the metal–cyclobutane complexes, which form carbene active centres on dissociation[68]:



(23)

This served as a basis for the hypothesis that metal–cyclobutane intermediates are involved in the chain metathetical process, which is hardly justified, since metal–cyclobutane

complexes are relatively stable and chain propagation in metathetical reactions proceeds at enormous rates.

The unusual metathetical reactions of olefinic and acetylenic hydrocarbons have attracted the attention of investigators to a new class of active centres arising in the chemical reactions—the carbene and carbyne complexes of transition metals. In many instances they are apparently intermediates in the catalytic reactions of hydrocarbons.

IV. THE MECHANISMS OF THE ELEMENTARY STEPS IN THE CATALYTIC REACTIONS OF HYDROCARBONS UNDER THE INFLUENCE OF TRANSITION METAL COMPOUNDS

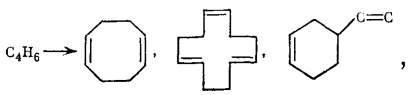
It is well known that many catalytic reactions of hydrocarbons proceed at low temperatures via stages involving organometallic compounds. Apart from the polymerisation of olefins, dienes, and their derivatives, one may quote instances of many other reactions in which the formation of organometallic intermediates has been established. For example, the dimerisation (linear oligomerisation) proceeds via consecutive stages involving the formation of HMX and the corresponding organometallic compound[69,70]:

$$HNiX + H_2C{=}CH_2 \rightleftarrows CH_3CH_2NiX \xrightarrow{C_2H_4} CH_3CH_2CH_2CH_2NiX \rightarrow C_2H_5HC{=}CH_2 + HNiX \quad (24a)$$

$$HNiX + H_2C{=}CH \rightleftarrows \underset{\displaystyle C_6H_5}{CH_2CHNiX} \xrightarrow{H_2C=CH-C_6H_5} \quad (24b)$$

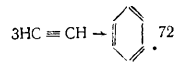
$$CH_3\underset{\displaystyle C_6H_5}{CH}CH_2-\underset{\displaystyle C_6H_5}{CH}NiX \rightarrow CH_3\underset{\displaystyle C_6H_5}{CH}-\underset{\displaystyle C_6H_5}{CH}=CH + HNiX \ .$$

Other reactions, in particular the cyclic oligomerisation of olefins, dienes, and acetylenic compounds under the influence of reduced transition metal (Ni, Co, Ti, etc.) compounds (the formation of vinylcyclohexene, cyclo-octadiene, cyclododecadiene, aromatic derivatives of acetylenic compounds, etc.), proceed cooperatively at a transition metal atom, sometimes without explicit stages with formation of organometallic σ-compounds,



(25a)

linear dimers and trimers being produced[71]:



(25b)

The same applies to the dienylation reactions occurring under the influence of reduced cobalt, palladium, rhodium, etc. compounds (see, for example, Müller et al.[73]):

$$H_2C{=}CHCH{=}CH_2 + \underset{\displaystyle COOR}{H_2C{=}CH} \rightarrow H_2C{=}CHCH{-}\underset{\displaystyle COOR}{CHCH_2CH_2} \ ; \quad (26a)$$

$$H_2C{=}CHCH{=}CH_2 + C_2H_4 \rightarrow CH_3CH{=}CHCH_2CH{=}CH_2 \ ; \quad (26b)$$

$$2H_2C{=}CHCH{=}CH_2 \xrightarrow{Pd} H_2C{=}CHCH-\underset{\displaystyle CH_3}{CH}{=}CHCH{=}CH_2 \ . \quad (26c)$$

All the above reactions take place with migration of a hydrogen atom.

The oxo synthesis under the influence of cobalt and rhodium compounds is also related to reactions proceeding via stages with formation of organometallic compounds[74,75]:

$$HCo(CO)_3 + C_2H_4 \rightarrow CH_3CH_2Co(CO)_3 \xrightarrow{CO} CH_3CH_2COCo(CO)_3 \rightarrow$$

$$\xrightarrow{H_2} CH_3CH_2C\overset{H}{\underset{O}{\diagdown\!\!\diagup}} + HCo(CO)_3 \ . \quad (27)$$

Many other catalytic reactions of hydrocarbons under the influence of transition metals at elevated temperatures should proceed, according to their character, via stages involving the formation of organometallic compounds. This applies to the dehydrogenation, hydrogenation, skeletal isomerisation, and hydrogenolysis of hydrocarbons.

The pathways in the chemical reactions involved in heterogeneous catalysis are usually represented by pathway mechanisms which are convenient for the kinetic description of the process but in many instances fail to elucidate the chemical significance of the elementary steps. The study of the mechanisms of the reactions of organometallic compounds in model systems can apparently yield additional information about the chemical nature of the individual stages of the reaction. On the basis of experimental data on the decomposition pathways of organometallic compounds of transition metals, it is possible to consider the chemical nature of the hydrogenolysis and isomerisation of the carbon skeleton via stages involving the formation of carbene species and cyclopropane derivatives respectively.

1. Hydrogenolysis and Skeletal Isomerisation of Hydrocarbons

The mechanisms of hydrogenolysis usually employed involve the adsorption of adjacent carbon atoms on adjacent metal atoms with dissociation of the C–H bond. It is assumed that the dissociation of the C–C bonds requires that the hydrocarbon groups linked to the metal must undergo further dehydrogenation up to the complete elimination of hydrogen from the carbon atoms[76–78] in $-CH_2C-C$ (with the ruptured bonds to M M) fragments are then hydrogenated. The hydrogenolysis belongs to the type of catalytic reactions which are believed to require the simultaneous involvement of a complex *ensemble* of active centres in the reaction. Furthermore the metathetical reaction of olefins indicates the possibility of its occurrence in the presence of hydrogen at one of the metal atoms:

$$RHC{=}MX_n + H_2 \rightarrow RCH_3 + MX_n \ (\text{or } H_2MX_n) \quad (28)$$

As studies on metathetical reactions have developed, it has become clear that almost all transition metals can take part in them. The catalysts of metathesis are usually believed to be only those metals (Mo, W, Re, Ta) in the presence of which the reaction proceeds with a long chain. For the metals indicated, the chain length reaches 10^6–10^7. Although the formation of carbene species is characteristic of almost all other transition metals, the metathetical reactions in their presence do not occur or develop with a short chain.

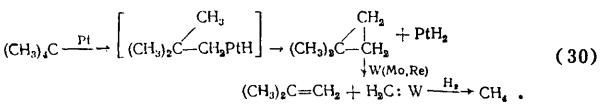
Free carbons in solution combine at the instant of formation with a hydrogen molecule[79]. It has been shown[80] that hydrogen adds at 49 °C to the stable carbene complex $(CO)_5W{=}C(C_6H_5)_2$. A similar reaction in the presence of deuterium should lead to the appearance of two deuterium atoms at a single carbon atom in the initial stage.

The activating effect of small amounts of reduced tungsten, rhenium, and molybdenum compounds in the hydrogenolysis of ethane and neopentane in the presence of a platinum catalyst[81,82] may be caused, as mentioned in our communications[83,84], by their activity in metathetical reactions. The fact that the first stage in the hydrogenolysis of paraffins involves the formation of C=C bonds is also correlated with this fact:

$$RCH_2CH_2R \underset{(a')}{\overset{Pt\ (a)}{\rightleftarrows}} H_2 + RHC{=}CHR \xrightarrow{(b)} \begin{cases} \xrightarrow{W\ \text{etc.}} RHC{=}W \\ \xrightarrow{Pt} RHC{=}Pt \end{cases} \xrightarrow{H_2} RCH_3 \ . \quad (29)$$

In the absence of tungsten, molybdenum, and rhenium compounds, the excess hydrogen retards the hydrogenolysis by shifting the equilibrium towards the starting material [reaction (29a')]. The decrease of the inhibiting effect of

hydrogen in the presence of the above metals is associated with the fact that the latter are more effective in metathetical reactions than platinum. The accelerating effect of tungsten and other metals active in metathetical reactions on the hydrogenolysis of neopentane under the influence of platinum agrees with the extremely effective decomposition of cyclopropane groups by metathetical catalysts:

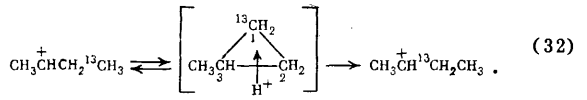


(30)

Numerous studies have been devoted to the skeletal isomerisation of hydrocarbons under the influence of cationic systems. It has been shown[85] that n-[1-^{13}C]butane isomerises rapidly to n-[2-^{13}C]butane under the influence of solutions of superacids (HF + SbF_5):

$$CH_3CH_2CH_2^{13}CH_3 \rightleftarrows CH_3CH_2^{13}CH_2CH_3 . \qquad (31)$$

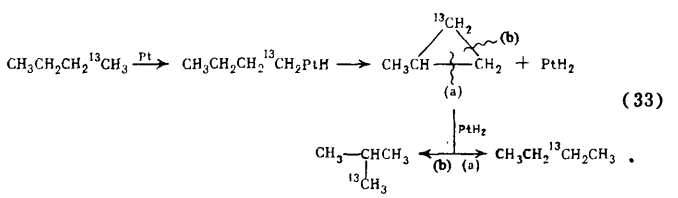
The rate of migration of the ^{13}C atom in n-butane is approximately equal to the rate of isomerisation of n-pentane to isopentane in the presence of the same catalyst. It has been suggested[85] that protonated cyclopropane, which can be formed from a classical carbonium ion, is an intermediate:



(32)

The addition of H^+ to the carbon atom (1) with dissociation of the C(1)–C(3) bond leads to the reformation of the initial cation; the addition of H^+ to the C(2) atom with dissociation of the C(2)–C(3) bond leads to the formation of a carbon skeleton with migration of ^{13}C to a neighbouring position; on the other hand, the addition of H^+ to the C(1) atom with dissociation of the C(1)–C(2) bond results in the formation of an iso-skeleton with the ^{13}C atom in the methyl group. These ideas were used to explain the mechanism of the rapid skeletal isomerisation of n-pentane to isopentane under the influence of cationic systems[86]. The nature of the intermediate state, consisting of protonated cyclopropanes, has been examined[87–89].

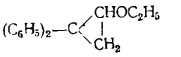
Cyclopropane derivatives can be formed also in the α-decomposition of the organometallic compound. This apparently determines the possibility of skeletal isomerisation also in the presence of non-acid catalysts. It has been established[90] that n-[1-^{13}C]butane is converted on platinum films into isobutane (containing the label only in the methyl group) and n-[2-^{13}C]butane, the isobutane/n-[2-^{13}C]butane ratio remaining constant in the course of the reaction. Hence it follows that the above product should arise from a single intermediate. Thus the above migration of the ^{13}C atom on acid catalysts is also possible on metallic catalysts without cationic components. Such reactions can proceed via stages involving the formation of an organometallic compound with subsequent formation of the cyclopropane ring:



(33)

The usual reactions (decomposition of diazo-compounds etc.) leading to carbene species in solution are as a rule accompanied by the formation of cyclopropane derivatives and olefins (iso-olefins), which arise also as a result of the decomposition of the cyclopropane derivatives formed as the primary products. The ratio of the cyclopropane derivatives and olefins depends in the first place on the structure of the carbene and to a certain extent on the method of its synthesis. According to the data quoted by Kirmse[91], the yields of cyclopropane derivatives are as follows for different carbenes (expressed in percentages of the theoretical yield): 80–96% for $(CH_3)_3CCH$:, 25–51% for $(CH_3)_2CHCH$:, 41% for $C_2H_5CH(CH)_3CH$:, and 43–65% for $(CH_3)_3C-C(CH_3)$:.

So far there are no data on the specific character of the reactions of carbene complexes of transition metals, but one may expect that the ability to form cyclopropane derivatives will also be manifested in such cases. The formation of cyclopropane and its derivatives in metathetical reactions has been noted in a number of studies[36,63,92]. Diphenylcarbenepentacarbonyltungsten reacts with ethyl vinyl ether to form the cyclopropane derivative



in 65% yield[93].

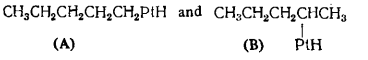
The reactions described above presuppose the primary formation of an organometallic compound via the oxidative addition of hydrocarbons to active zerovalent metals. The possibility of such reactions is considered below. The reaction involving the isomerisation of n-pentane to isopentane, which is the starting material for the synthesis of isoprene, has been studied in a number of investigations. In order to account for the mechanism of this process in the presence of a platinum/alumina catalyst, the following pathway mechanism has been proposed[94]:

$$n\text{-}C_5H_{12} + 2Z_1 \rightarrow C_5H_{11}Z_1 + HZ_1 ; \qquad (34a)$$

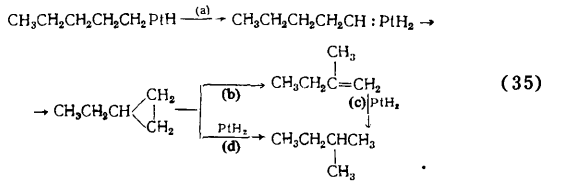
$$C_5H_{11}Z_1 + Z_2 \rightarrow C_5H_{11}Z_2 ; \qquad (34b)$$

$$C_5H_{11}Z_2 \xrightarrow{H_2} \text{iso-}C_5H_{12} . \qquad (34c)$$

The mechanism presupposes the presence of two types of active centres on the catalyst (Z_1 and Z_2). A group of the type of an organometallic compound arises in reaction (34a), while in reaction (34b) the group [C_5H_{11}] is transferred to the active centre Z_2 on which the isomerisation step takes place with participation of hydrogen. The chemical significance of this stage of the reaction as well as the role of hydrogen in it remain obscure. In the absence of a considerable excess of hydrogen (5–10 moles per mole of pentane) the catalyst becomes covered in coke and is rapidly deactivated. In the discussion the chemical nature of the dehydrogenation reactions of hydrocarbons, arguments are adduced below in favour of the initial occurrence of the oxidative addition of hydrocarbons to the metal. For the reactions considered, the primary step may lead to organometallic compounds of two types:

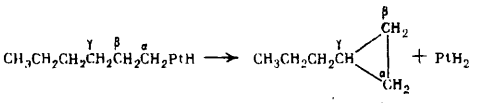


The main pathway in the decomposition of the compounds indicated (β-disproportionation) leads to pentene with a normal carbon skeleton, while α-decomposition, accompanied by the formation of carbene species can lead to the isomerisation of the carbon skeleton:



(35)

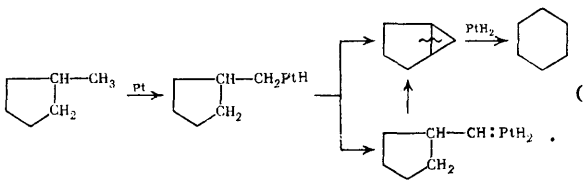
One cannot rule out the possibility of the formation of cyclopropane derivatives as a result of a γ-elimination reaction, as noted by Davidson et al.[16]



(36)

On the basis of the mechanism proposed, the saturation of the catalyst with coke can be accounted for by the formation of an extremely reactive analogue of isobutene, namely $CH_3CH_2C(CH_3)=CH_2$. Hydrogen converts it into isopentane, which prevents the saturation of the catalyst with coke.

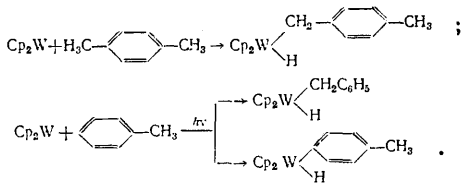
The mechanism of the reversible isomerisation of methylcyclopentane to cyclohexane in the presence of a platinum catalyst can be treated analogously. In the given instance the reaction also requires a considerable excess of hydrogen:



(37)

2. Dehydrogenation of Hydrocarbons

The reaction involving oxidative addition to reduced forms of metals is nowadays well known. The addition of alkenyl halides to nickel carbonyl has been used[95] to obtain the corresponding π-allyl complexes. Alkyl and alkenyl halides readily add to arene complexes of zerovalent vanadium[96] with formation of primary organometallic derivatives. Green has shown[97] that *p*-xylene adds to biscyclopentadienyltungsten even at 60 °C, while toluene reacts with the latter at the usual temperature under the influence of light in accordance with the equation



(38)

The oxidative addition of triphenylphosphine to zerovalent metals (Pd, Ir, Rh, Pt) has been described[98–100]:

$$Ph_3P + Pd^0 \rightarrow Ph_2P{-}Pd{-}Ph \ . \qquad (39)$$

Since the least coordination saturated metal atoms, located on the crystal faces and in the defects, participate preferentially in the dehydrogenation reactions of hydrocarbons, it may be expected that at high temperatures the primary step is oxidative addition accompanied by the formation of an organometallic compound, since decomposition leads to the dehydrogenation products:

$$CH_3CH_2CH_2CH_3 + M^0 \rightarrow CH_3CH_2CH_2CH_2MH \rightleftarrows CH_3CH_2CH{=}CH_2 + MH_2 \ ; \qquad (40a)$$

$$C_6H_5CH_2CH_3 + M^0 \rightarrow C_6H_5\underset{\displaystyle MH}{\underset{|}{C}}HCH_3 \rightleftarrows C_6H_5CH{=}CH_2 + MH_2 \ ; \qquad (40b)$$

$$CH_3CH_2CH_2CH{=}CHR + M^0 \rightarrow CH_3CH_2\underset{\displaystyle MH}{\underset{|}{C}}HCH{=}CHR \rightleftarrows$$

$$\rightleftarrows CH_3CH{=}CHCH{=}CHR + MH_2 \ . \qquad (40c)$$

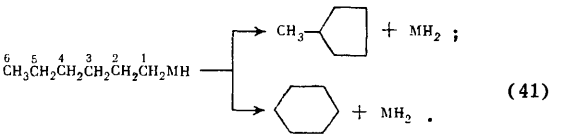
The oxidative addition of butane [reaction (40a)] takes place most readily with participation of the methyl group, since this entails the formation of a more stable primary organometallic compound and the dehydrogenation step involves the usual decomposition pathway of alkyl derivatives (β-decomposition). The finding that the primary product of the dehydrogenation of butane is α-butene, which isomerises further to β-butenes, is consistent with the above considerations. In the case of paraffins containing a large number of CH_2 groups, the fraction of such groups participating in the oxidative addition step increases, which leads to the primary formation of inner double bonds.

The reaction of benzene derivatives [reaction (40b)] takes place with participation of the α-methylene group, since this results in the formation of a more stable compound in which the C–M bond is conjugated with the benzene ring. This fact is correlated with the finding that the α-methylene group at the benzene ring is the first to undergo deuterium exchange under dehydrogenation conditions (deuterium adds to the C–M bond).

In unsaturated hydrocarbons the α-methylene group at the double bond is most reactive, which leads to the π-allyl coordination of the olefin to the transition metal in the primary step. As a consequence of the migration of the double bonds in the allyl system, all the hydrogen atoms are involved in deuterium exchange.

In all the examples presented the dehydrogenation mechanism reflects the main pathway in the decomposition of alkyl and a number of aryl derivatives of organometallic compounds of transition metals—β-decomposition. The mechanism of the dehydrogenation of hydrocarbons at a single metal atom as a result of β-decomposition operates most explicitly in the thoroughly investigated dimerisation (oligomerisation) reactions of ethylene, styrene, and other olefins[69,70]. The decomposition of organolithium and organoaluminium compounds at comparatively low temperatures with formation of olefins and metal hydrides proceeds analogously.

The possible decomposition pathways become more complex with increase in the length of the carbon skeleton. The mechanism under discussion for hydrocarbons becomes just as probable for the reaction at the C–H bond of the fifth or sixth carbon atom, starting from C_5 (and particularly C_6) hydrocarbons:



(41)

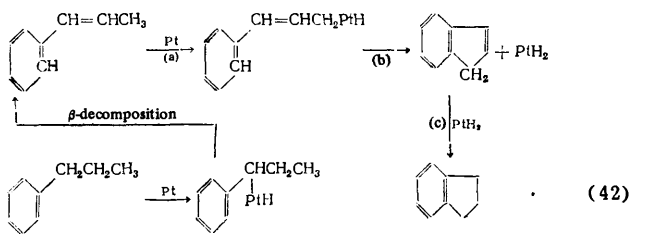
The abstraction of a hydrogen atom from C(5) and C(6) does not entail steric hindrance, while the abstraction of hydrogen atoms from C(3) and C(4) is accompanied by the formation of strained three- and four-membered rings. The contribution of α-decomposition, leading to carbene complexes, is extremely small for alkyl derivatives. One cannot rule out the possibility that the mechanism described reflects the mechanism of the dehydrocyclisation of hexane to methylcyclopentane.

The α-decomposition of organometallic compounds becomes possible in those cases where the reaction leads to the formation of a relatively stable carbene complex, for example, in the dehydrogenation of alkyl ethers, dialkyl sulphides, tetramethylsilane, etc.

It was shown above that the carbene pathway leading to the decomposition of organometallic compounds of platinum, palladium, and many other metals predominates when these have no β-hydrogen atoms. Such a decomposition pathway

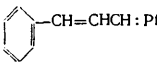
is apparently rate-determining in the dehydrogenation of toluene, tetramethylsilane, neopentane, etc. when the removal of hydrogen from the system is ensured. The oxidative addition of toluene to a zerovalent metal should lead to the formation of bibenzyl.

The main initial products of the reactions of n-propylbenzene and ω-methylstyrene in the presence of Pt/Al_2O_3 at 450–500 °C are indene and indan, while the formation of other products (the hydrogenolysis and isomerisation products) is associated with the reactions of intermediates[101]. The CH_3 group in ω-methylstyrene and the α-methylene group in n-propylbenzene should be extremely reactive in oxidative addition to platinum. It is therefore possible to consider a reaction mechanism involving oxidative addition stages, which leads to one intermediate:



(42)

Reaction (42) can proceed via ω-elimination or via a stage in which a carbene species is formed:



3. Hydrogenation of Olefins

The addition of olefinic and diene hydrocarbons to a hydrogen-transition metal bond is known to occur in many instances. Nickel, cobalt, and chromium hydrides in ether combine with butadiene to form π-allyl complexes, which dissolve[102]:

$$\begin{aligned} NiH_2 &\xrightarrow{C_4H_6} (\pi\text{-}C_4H_7)_2Ni \ ; \\ CoH_n &\xrightarrow{C_4H_6} (\pi\text{-}C_4H_7)_3Co \ ; \\ CrH_3 &\xrightarrow{C_4H_6} (\pi\text{-}C_4H_7)_3Cr \ . \end{aligned} \qquad (43)$$

As mentioned above, the dimerisation reactions of ethylene and styrene proceed via a stage in which the olefin adds to HNiX. In the polymerisation of dienes and olefins under the influence of Ziegler–Natta systems containing titanium, cobalt, nickel, and other metal halides as well as organoaluminium compounds, hydrogen is used as the chain transferring agent:

$$pCH_2MX + H_2 \rightarrow pCH_3 + HMX \xrightarrow{\text{olefin}} RMX \ . \qquad (44)$$

Thus there are sufficient grounds to assume that the first stage in the hydrogenation reaction is the addition of the olefin to the M–H bond with formation of an organometallic derivative. This is consistent with the concept of the semihydrogenated state adopted in catalysis. On the basis of the available data for the reaction pathways of organometallic compounds of transition metals, the hydrogenation mechanism can be represented as follows in relation to metal dihydrides:

$$H{-}M{-}H + 2H_2C{=}CHR \rightarrow RCH_2CH_2MCH_2CH_2R \rightarrow$$

$$\begin{cases} \xrightarrow{2H_2} 2RCH_2CH_3 + H{-}M{-}H \ ; & (45a) \\ \rightarrow RHC{=}CH_2 + RCH_2CH_3 \ ; & (45b) \\ \rightarrow RCH_2CH_3 + RCH_2CH : M \xrightarrow{D_2} RCH_2CHD_2 \ ; & (45c) \\ \rightarrow RCH_2CH_2CH_2CH_2R \ . & (45d) \end{cases}$$

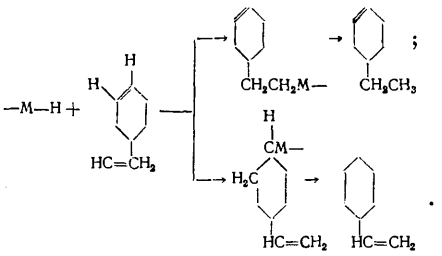
Reaction (45a) leads to the hydrogenation of both olefinic molecules. Reaction (45b), which proceeds via the β-decomposition mechanism, regenerates one olefinic molecule. The contribution of reaction (45c) can increase on formation of relatively more stable carbenes and can be estimated from the number of molecules containing two deuterium atoms at a single carbon atom at low conversions.

The semihydrogenated state in the case of styrene, 1,1-diphenylethylene, or compounds of the type of alkyl vinyl ethers and acrylonitrile corresponds to an addition product in which the C–M bond is conjugated with the benzene ring or other groups:

$$\begin{aligned} &{-}M{-}H + C_6H_5HC{=}CH_2 \rightarrow {-}M{-}\underset{C_6H_5}{CHCH_3} \ ; \\ &{-}M{-}H + (C_6H_5)_2C{=}CH_2 \rightarrow {-}M{-}\underset{(C_6H_5)}{C}{-}CH_3 \ ; \\ &{-}M{-}H + H_2C{=}CHOR \rightarrow {-}M{-}\underset{OR}{CHCH_3} \ ; \\ &{-}M{-}H + H_2C{=}\underset{CN}{CH} \rightarrow {-}M{-}\underset{CN}{CH}{-}CH_3 \ . \end{aligned} \qquad (46)$$

This mode of addition of styrene to HNiX has been demonstrated[70].

It has been shown that, in the hydrogenation of vinylcyclohexene derivatives over platinum and nickel, the vinyl group is hydrogenated faster than the double bond in the cyclohexene ring[103]:

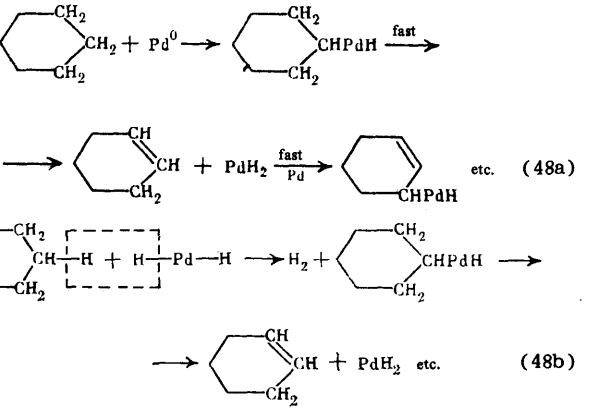


(47a)

(47b)

Pathway (47a) leads to the formation of a more stable primary organometallic compound than pathway (47b). For the same reason, the hydrogenation of α-olefins is always faster than that of olefins with inner double bonds.

The accelerating effect of a small amount of hydrogen on the dehydrogenation of cyclohexane in the presence of a palladium catalyst has been noted[104]. These somewhat unexpected results can be explained by considering two reaction pathways via stages involving the formation of organometallic compounds:

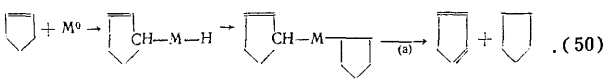


If reaction (48b) is faster than (48a), then the activating effect of hydrogen can apparently be explained by the formation of the hydride PdH_2, which accelerates the stage in which the organometallic compound is formed.

The autohydrogenation phenomenon, observed in the reactions of ethylene, butadiene, and cyclopentene over nickel, palladium, and iron[105–108] can be explained solely in terms of organometallic intermediates:

$$H_2C{=}CH_2 + M^0 \rightarrow H_2C{=}CH{-}M{-}H \xrightarrow[(a)]{C_2H_4} H_2C{=}CH{-}M{-}CH_2CH_3 \rightarrow \rightarrow HC{\equiv}CH + CH_3CH_3 \ . \quad (49)$$

Analogous subsequent reactions of acetylene lead to the formation of carbide species:



. (50)

The above equations presuppose the consecutive occurrence of the reaction via stages involving oxidative addition to the zerovalent metal (M^0), the addition of the olefin to the M–H bond, and the β-decomposition of the organometallic compound. Numerous examples of deuterium exchange involving olefins and dienes, observed in hydrogenation with deuterium[108], are consistent with the above ideas:

$$H_2C{=}CH_2 + D{-}M{-}D \rightarrow CH_2D{-}CH_2MCH_2CH_2D \xrightarrow[\beta\text{-decomposition}]{} HDC{=}CH_2 + CH_3CH_2D \ . \quad (51)$$

Reactions (49) and (50) lead to analogous products of single-stage exchange in olefins and dienes if deuterium adds to the C–M bond in stages (a).

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Thus studies of the composition of the decomposition products of methyl, benzyl, trimethylsilylmethyl, and certain other derivatives of transition metals (Mo, W, Re, Ta, Pt, Pd, Cr, Rh, Nd, Y, Nb) established that the main pathway leading to the decomposition of the above organometallic compounds at the instant of their formation is α-decomposition accompanied by the formation of carbene and carbyne species. The absence of radical stages in the decomposition of the above compounds has been demonstrated.

The metathetical reactions of olefins and the ring opening reactions of cyclo-olefins proceed via a chain mechanism under the influence of carbene complexes of transition metals. The mechanisms of the elementary stages of the process, namely initiation, chain propagation, and chain transfer, have been examined. It has been established that the above reactions obey the usual rules characteristic of chain processes.

Analysis of experimental data for the reaction pathways of organometallic compounds of transition metals led to hypotheses concerning the chemical nature of the elementary steps in the catalytic reactions of hydrocarbons at a single metal atom. It has been suggested that the hydrogenolysis of the carbon skeleton proceeds via consecutive stages involving dehydrogenation (the formation of C=C bonds), the formation of carbene complexes, and addition of hydrogen to the latter.

The skeletal isomerisation reactions proceed via a stage in which cyclopropane groups are formed. The mechanism of the dehydrogenation reaction includes a stage involving the oxidative addition of the hydrocarbon to a zerovalent metal followed by the β-decomposition of the organometallic compound.

A two-stage mechanism, providing for the addition of the olefin to the M–H bond and of hydrogen to the C–M bond, has been proposed for the hydrogenation reactions. The above considerations explain the mechanism of the autohydration reactions. The above considerations explain the mechanism of the autohydrogenation of olefins and dienes and the mechanism of the deuterium exchange involving such compounds.

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The Mechanism of the C_5- and C_6-Dehydrocyclisation and Skeletal Isomerisation Reactions of Hydrocarbons in the Presence of Metal-Containing catalysts

O.V.Bragin and S.A.Krasavin

A systematic account is given of data on the most important reactions of hydrocarbons in the presence of metal-containing catalysts. The modern ideas concerning the mechanisms of the isomerisation and C_5- and C_6-dehydrocyclisation of alkanes are described. The role of hydrogen in these reactions in the presence of metal-containing and in the first place platinum catalysts is analysed. The influence of the structure of metallic catalysts on the mechanisms of the dehydrocyclisation of skeletal isomerisation reactions of alkanes is examined.
The bibliography includes 170 references.

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I. INTRODUCTION

The dehydrocyclisation and isomerisation of hydrocarbons are some of the most important processes in organic and petrochemical synthesis. More than half of the aromatic hydrocarbons are obtained nowadays from petroleum raw materials with the aid of dehydrocyclisation (DHC), dehydrogenation, and dehydroisomerisation reactions. It is therefore natural that these processes have been investigated most vigorously during the last decade.

The DHC reactions are divided into two types—C_5- and C_6-DHC. This classification is based on the different natures of the hydrocarbons formed, the considerable differences between the mechanisms of the reactions, and finally, in many instances, the differences between the catalysts employed. C_5-DHC results in the formation of cyclopentane hydrocarbons or a new five-membered ring in condensed systems; C_6-DHC leads to the formation of aromatic (mono- or poly-nuclear) hydrocarbons.

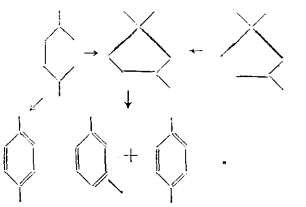
It is noteworthy that both types of DHC, in the presence of both metallic and oxide catalysts, were discovered in the Soviet Union[1-4]. The work of D.A.Kazanskii and his co-workers has made a particularly large contribution to the investigation of DHC reactions. These and certain subsequent researches into C_5- and C_6-DHC were described in monographs and reviews[5-11]. However, the problems of the interrelation between the C_5- and C_6-DHC reactions of alkanes, the specific details of the mechanisms of both types of cyclisation, the skeletal isomerisation reactions of alkanes and the hydrogenolysis of cyclopentanes, which are closely related to the above processes, and finally the involvement and role of hydrogen in these reactions merit special consideration.

II. CATALYTIC REACTIONS OF ALKANES AND CYCLOPENTANES IN THE PRESENCE OF PLATINUM CATALYSTS

C_6-Dehydrocyclisation of Alkanes

In the majority of studies in the presence of various metallic and in the first place platinum catalysts the C_5- and C_6-DHC reactions were investigated jointly because their conditions are very similar. In the first studies on reforming[9] the possibility of the intermediate formation of cyclopentane in the aromatisation of n-pentane was pointed out, because the catalytic reaction mixture contained a certain amount of alkylcyclopentanes.

Subsequently, this aromatisation pathway received a rigorous experimental confirmation, particularly as a result of the study of the reactions of 2,5-dimethylhexane, 2,2,4-trimethylpentane, and 1,1,3-trimethylcyclopentane in the presence of various platinum catalysts:



It was found that, in the presence of monofunctional platinum catalysts, 2,2,4-trimethylpentane as well as 1,1,3-trimethylcyclopentane give rise to approximately equal amounts of *m*- and *p*-xylenes[12-15], i.e. the aromatisation proceeds via

the intermediate formation of a C_5 ring. It has been suggested[15] that the rate-limiting stage in C_6-DHC involves the expansion of the five-membered ring. On the other hand, the main product of the aromatisation of 2,5-dimethylhexane is *p*-xylene, which shows that the C_5- and C_6-DHC reactions take place simultaneously and independently. Thus the pathway followed in the aromatisation proceeds depends significantly on the structure of the initial alkane.

The possibility of the direct 1,6-ring closure in the presence of Pt/C and various Pt/Al_2O_3 catalysts has been discussed[5,14,16-19]. This conclusion is based on the reactions of 2,2- and 3,3-dimethylhexanes[17,20], which partially cyclise to *gem*-dimethylcyclohexane and the latter is in its turn dehydrogenated under the experimental conditions with formation of aromatic hydrocarbons. An analogous alkane aromatisation pathway was discussed by Ivan'kovich et al.[21] The results of the study of the C_6-dehydrocyclisation of n-[1-^{14}C]- and n-[4-^{14}C]-heptanes have been analysed in detail[16].

On the other hand, Paal and Tetenyi[22-24] concluded that n-hexane undergoes successive dehydrogenation to a triene in the presence of nickel and platinum catalysts with subsequent cyclisation and aromatisation. This reaction mechanism and the absence of intermediate cyclohexane and cyclohexene in the reaction chain were confirmed by the same workers by introducing the ^{14}C label. Kazanskii and co-workers[25-28] reached an analogous conclusion concerning the n-alkane aromatisation pathways in the presence of Pt, Pt/Al_2O_3, and Pt/C catalysts.

Thus it can be assumed that the aromatisation of n-alkanes proceeds via intermediate dehydrogenation stages. At the same time, alkanes with a quaternary carbon atom cannot be dehydrogenated quite so readily under the reaction conditions and their aromatisation proceeds at least partially via the direct "cyclohexane" mechanism.

Analysis of data on aromatic C_7-hydrocarbons in the presence of Pt/Al_2O_3 [29,30] demonstrated yet another possibility for the formation of aromatic hydrocarbons from alkanes—namely as a result of the primary formation of a C_7 ring and its subsequent contraction. This is indicated by the formation of small amounts of cycloheptane from ethylcyclopentane and by the position of the ^{14}C label in the [1-^{14}C]heptane aromatisation products.

Under real conditions of catalysis, the aromatisation of alkanes in the presence of metal-containing catalysts apparently proceeds via all the mechanisms indicated above. One of these may predominate to a significant extent depending on the structure of the initial hydrocarbon, the reaction conditions (the temperature and the carrier gas), the chemical composition of the catalyst, etc. Thus it has been stated that, with decrease of the acidity of the platinum/alumina catalyst[32-35] and with increase of temperature[36], the contribution of the C_5-dehydrocyclisation to the aromatisation process diminishes. In the presence of the Pt/Al_2O_3 catalysts the dehydroisomerisation reaction plays an appreciably greater role in aromatisation than in the presence of the palladium catalyst[9].

The C_6-DHC of n-hexane in the presence of platinum deposited on "non-acid" Al_2O_3 has been investigated[14]. The authors suggested that the reaction proceeds via two pathways: (a) via consecutive mechanism involving the dehydrogenation and subsequent cyclisation of a triene and (b) via the direct aromatisation of n-hexane. The important role of hydrogen in the reaction and the undoubted dependence of the aromatisation mechanism on the hydrogen pressure in the reaction mixture were noted.

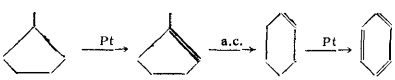
The results of studies of the aromatisation of n-heptane in the presence of Pt/Al_2O_3 catalysts by the thermal desorption and kinetic methods are of undoubted interest[37-39]. The temperature ranges of the desorption process and the number of active centres were determined. It was suggested that at least two types of platinum active centres are present on the surface of the Pt/Al_2O_3 catalyst. According to the authors[37-39], the C_6-DHC reaction takes place predominantly on one of them with formation of toluene, while the second type of centres are characterised by a greater activity in relation to the dissociation of the C–C bond and lead to the formation of benzene from toluene. The authors suggest that one of the two types of catalytically active centres is associated with the existence of crystalline platinum and the other with platinum complexes; the latter may also consist of cluster formations whose composition includes aluminium ions and OH groups as well. Overall, the results presented are in good agreement with the consecutive aromatisation mechanism. The authors[37-39] point out the possibility that the reaction rate is limited by the stage involving the desorption of the superdehydrogenated forms of aromatic compounds (with participation of hydrogen) on centres of one of the types. On centres of the other type the reaction rate is limited by the dehydrogenation stage[39].

As shown above, one of the pathways leading to the formation of aromatic hydrocarbons from alkanes is dehydroisomerisation of the intermediate alkylcyclopentanes.

Dehydroisomerisation of Cyclopentanes

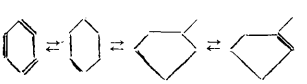
It has been shown by the kinetic isotope method[40] that, in the presence of Pt/C at 310 °C in a stream of helium, benzene is not formed from n-hexane via methylcyclopentane. The methylcyclopentane dehydroisomerisation reaction is suppressed under these conditions. Under other conditions (550 °C, p_{H_2} = 2.25 atm), it was established by the same method[25] that approximately 20% of benzene is formed from hexane via methylcyclopentane in the presence of the platinum/alumina catalyst, the rate of formation of benzene from methylcyclopentadiene being significantly higher than the rate of its formation from methylcyclopentane and methylcyclopentenes. On this basis, it is suggested that the C_6 ring is formed after the dehydrogenation of the cyclopentane hydrocarbon to methylcyclopentadiene.

In studies where the bifunctional character of dehydroisomerisation catalysts is emphasised, the occurrence of a process with participation of the acid centres (a.c.) of the carrier[34,35], for example via a carbonium ion mechanism[41-43], has been postulated:



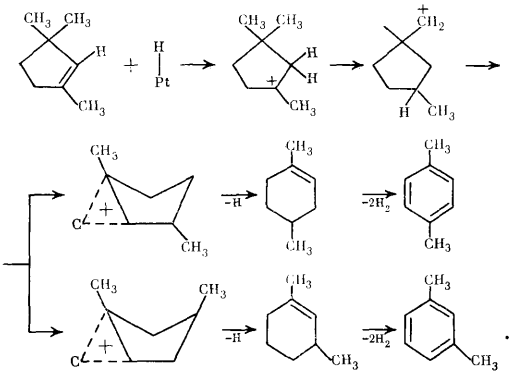
It has also been suggested that the dehydroisomerisation reaction proceeds at an active centre formed by a platinum atom or crystal and the adjoining acid centre[42].

The application of the kinetic isotope method made it possible to demonstrate that the dehydroisomerisation of methylcyclopentane in the presence of the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts under reforming conditions (480 °C, p_{H_2} = 20 atm) can take place also without the intermediate formation of a cyclene[44]:



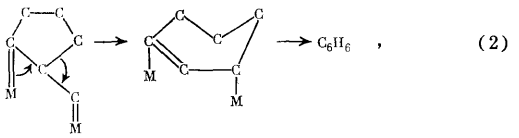
However, it is not clear which factor (hydrogen pressure, the acidity of the carrier, etc.) is involved in the discrepancy between the results of two studies by Isagulyants and co-workers[25,44].

The study of the dehydroisomerisation reaction in the presence of platinum/alumina catalysts with a suppressed acid function and also in the presence of a platinum film or platinum deposited on a relatively inert carrier (activated charcoal) demonstrated the possibility that the reaction takes place only at metallic centres. According to Lesger[15] the dehydroisomerisation mechanism consists in the formation of electron-deficient cyclopentyl rings on electron transfer from the semihydrogenated alkylcyclopentene to the platinum atom (functioning as a weak Lewis acid) accompanied by the 1,4-hydrogen shift or a series of 1,2-hydrogen shifts with subsequent ring expansion via a bicyclic intermediate:



(1)

It is emphasised[15] that the acid centres of the carrier of an industrial platinum/alumina catalyst may be more active in the isomerisation reaction than the platinum centres. According to the authors[8,15] the above mechanism (1) is preferable to the mechanism



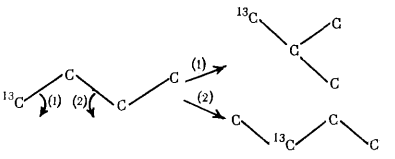
(2)

proposed by Muller and co-workers[13,45], according to which the preliminary abstraction of four hydrogen atoms is required. We may note that the proposed dehydroisomerisation mechanisms have overall features in common with the alkane isomerisation reaction.

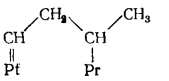
Isomerisation of Alkanes

The C_5-dehydrocyclisation and skeletal isomerisation reactions of alkanes as well as the hydrogenolysis and dehydroisomerisation of cyclopentanes in the presence of monofunctional catalysts are closely related and under certain conditions can occur simultaneously via parallel-consecutive mechanisms. Two main mechanisms of the isomerisation of alkanes in the presence of monofunctional platinum catalysts are distinguished at the present time[5,6]: the bond shift mechanism and the C_5-cyclic mechanism. However, despite the large number of studies carried out, there is as yet no unanimous view concerning the detailed reaction mechanism.

The bond shift mechanism was proposed to account for the characteristic features of the isomerisation of n-butane, isobutane, neopentane, and neohexane in the presence of sputtered platinum films[46,47].



Here (1) and (2) denote the possible directions of the bond shifts on formation of the corresponding product. Since isobutane and neopentane reacted at the same rates and with the same activation energies and the formation of a 1,2-diadsorbed or π-bonded intermediate cannot be postulated for neopentane, it has been suggested that the isomerisation proceeds via 1,3-adsorbed intermediate forms:



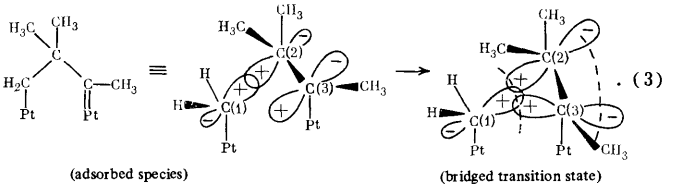
This structure of the adsorbed species is consistent also with data for the deuterolysis of 1,1-dimethylcyclopropane[13].

The study of the isomerisation reaction on oriented platinum films showed[47] that isobutane isomerises on the (111) face of a platinum single crystal more effectively than on the other faces, while for n-butane there are no great differences between the activities of different faces. This was explained by the possibility of the formation of a triadsorbed intermediate for isobutane on the platinum (111) face:



It is noteworthy that the isomerisation of neopentane is a structure-sensitive reaction[48]. Changes in the selectivity of the neopentane isomerisation as a function of the preliminary treatment of the catalyst and the degree of dispersion of the metal were explained on the basis of the characteristic features of the changes in the concentrations of triplets of platinum atoms and the corners and edges in polycrystalline platinum with increase in the size of crystallites. The possibility of three-point adsorption of neopentane on the platinum(111) face and the stepped platinum faces and the impossibility of such adsorption on the (110) and (100) faces were demonstrated with the aid of simple geometrical considerations.

The bond shift mechanism has been examined[49] from the standpoint of the molecular orbital method. The rearrangement of neohexane to 2-methylpentane can be represented as follows (henceforth referred to as Anderson's mechanism):

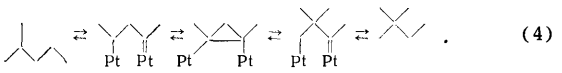


(adsorbed species) (bridged transition state)

(3)

It has been suggested that the electrons of the pπ orbital of the C(3) atom are partly displaced towards the metal, so that a structure intermediate between a carbonium ion and a radical is produced. Calculation of the energy of the bridge bond makes it possible to arrange alkanes in the sequence $n\text{-}C_4H_{10} < iso\text{-}C_4H_{10} < neo\text{-}C_5H_{12}$, which had been established previously[47] for the relative reactivities of these hydrocarbons in the presence of platinum. It has been noted[49] that,

whereas the sp^3 hybridisation of the C(2) atom does not prevent the isomerisation of neopentane, the sp^2 hybridisation of the C(3) atom [see mechanism (3)] to which the migrating group is transferred, rules out the possibility of the formation of neopentane from isopentane, which has been observed experimentally[47]. However, small but not negligible amounts of neohexane are formed from methylpentanes in the presence of platinum. It has been suggested[13] that in this case the isomerisation proceeds via the mechanism

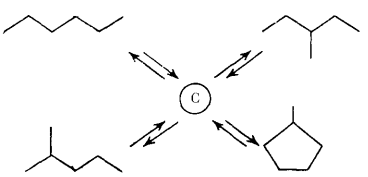


(4)

We may point out that the proportions of the products of the hydrogenolysis of methylcyclopropane observed experimentally[50] differ significantly from those of the butane isomerisation products[47]. The above mechanism can therefore be considered as one of the possible mechanisms of the isomerisation reaction only if it is assumed that the adsorbed cyclopropane is a transition state but not an intermediate in the reaction.

Thus the two bond shift isomerisation mechanisms examined differ mainly by the structure of the transition state. In both cases, firstly, the metal atom must be sufficiently electronegative and, secondly, the surface metal atoms must be capable of undergoing a rapid change in their valence in the rearrangement. The characteristic features of the catalytic action of iridium and platinum, which are the only Group VIII metals capable of catalysing the isomerisation of neopentane, have been treated from these standpoints[51]. For a long time it was impossible to observe the isomerisation of neopentane in the presence of palladium[47,51], although isobutane undergoes a rearrangement on palladium. It has only recently been reported[52] that neopentane can isomerise on an oriented palladium (111) film under the conditions of a high H_2/hydrocarbon ratio.

Isopentanes, n-hexane, and their homologues isomerise more readily than neopentane and neohexane in the presence of monofunctional platinum catalysts. Methylcyclopentane is then always formed, its concentration passing through a maximum with increase of the degree of conversion. It has been shown that methylcyclopentane and isomeric hexanes give identical initial proportions of the products (C_6 alkanes) on contact with the Pt/Al_2O_3 catalyst whose acidic function has been suppressed[45,53]. Analogous proportions of products are characteristic also of reactions in the presence of platinum deposited on activated charcoal and pumice and on platinum films, but they differ significantly from the proportions of the products obtained in the presence of explicitly bifunctional catalysts. On the basis of these findings, it has been suggested that there is a single transition complex in the isomerisation of hexanes and hydrogenolysis of methylcyclopentane in the presence of monofunctional platinum catalysts (the C_5-ring mechanism); the reactions of hydrocarbons are then represented schematically in the following manner[45]:



Here © represents a set of hydrocarbon interconversion products, some of which must have a cyclic structure, and the intermediates in the dehydrocyclisation reaction of alkanes are the same as in the hydrogenolysis of methylcyclopentane[54]. Thus the isomerisation and C_5 dehydrocyclisation reactions of alkanes, on the one hand, and the hydrogenolysis reactions of alkylcyclopentanes, on the other, are interrelated, which must be taken into account in explaining the structure of the interconversion products ©. We may note that the possibility of the isomerisation of alkanes as a result of the hydrogenolysis of an intermediate C_5-cyclic hydrocarbon was pointed out by Liberman et al.[55]

Hydrogenolysis of Cyclopentane

The hydrogenolysis of cyclopentane and its homologues has been most thoroughly investigated among this group of reactions. Detailed information about this process can be found in a number of communications[7,56-58]. Here we shall briefly discuss only the principal characteristic features and the proposed mechanisms of this reaction. The hydrogenolysis of cyclopentane hydrocarbons takes place successfully in the presence of platinum, rhodium, iridium, and osmium catalysts[59]. In the presence of platinum catalysts the hydrogenolysis slows down with increase of the number of substituents in the five-membered ring[58]. Data on the selectivity of the hydrogenolysis of substituted cyclopentanes via different pathways are of greatest importance. The selectivity depends on a number of factors: the size, number, and location of the substituents in the C_5 ring[58,60], the partial pressure and surface concentration of hydrogen†,[59,61] and the degree of dispersion of the metal[62-64].

Thus an increase of the partial pressure of hydrogen from 10 to 50 atm decreases the 2-methylpentane/n-hexane ratio in the hydrogenolysis of methylcyclopentane in the presence of different platinum catalysts[61]. It is of interest to note that at 50 atm in the presence of the 0.3% Pt/Al_2O_3 catalyst the tertiary-secondary C–C bonds are exclusively ruptured in the five-membered ring. It has been suggested[61-65] that the pathway followed in the hydrogenolysis of the C_5 ring is determined by the structure of the monoadsorbed complex, which depends on the relative contributions of two factors: the distribution of electron density in the alkylcyclopentane molecule and the electrophilicity (electron-donating properties) of the transition metal atoms in the catalyst, which is influenced by the hydrogen pressure. The influence of the hydrogen pressure on the pathway in the cyclisation of n-octane, namely an increase of the yield of 1,2-ethylmethylcyclopentane relative to propylcyclopentane with increase of hydrogen pressure, has been treated from the same standpoint[66]. However, the role of the carrier in the hydrogenolysis of alkylcyclopentanes remains obscure. The preferential dissociation of the tertiary-secondary C–C bonds in the C_5 ring can be logically explained on the assumption[67,68] that the hydrogenolysis of alkylcyclopentanes takes place preferentially at the acid centres of the 0.3% Pt/Al_2O_3 catalyst at a hydrogen pressure of 50 atm.

In his study of the influence of the platinum concentration in platinum/alumina catalysts on the hydrogenolysis of methylcyclobutane and methylcyclopentane, Gault[63] concluded that there are at least two hydrogenolysis mechanisms: the selective mechanism in which only the bonds between the secondary carbon atoms in the ring are ruptured and the non-selective mechanism leading to the equally probable dissociation of all the ring C–C bonds. The first mechanism is characteristic of the reaction on platinum films at low temperatures and in the presence of the 10% Pt/Al_2O_3 catalyst. The second

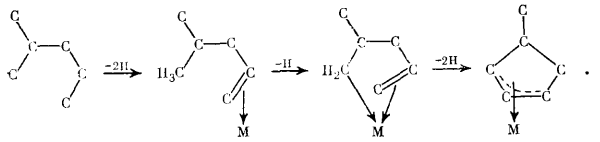
†See also C.Corolleur, F.G.Gault, and L.Beránek, React. Kinet.Catal.Letters, 1976, 5, 459.

mechanism operates on platinum films at high temperatures and in the presence of the 0.2% Pt/Al_2O_3 catalyst; in this case the proportions of the products are independent of the degree of conversion[62]. It has been suggested that the hydrogenolysis via the non-selective mechanism proceeds via the intermediate formation of α, β, γ-triadsorbed (π-bonded) species, while the reaction via the selective mechanism proceeds via α, α, β, β-tetra-adsorbed species. In the former case the plane of the ring is parallel and in the latter case perpendicular to the surface of the metal. The principal features of the selectivity of the hydrogenolysis of various cyclic hydrocarbons can be logically explained from the above standpoints. For example, an increase of the partial pressure of hydrogen should suppress the formation of the tetra-adsorbed species, i.e. should diminish the contribution of the selective mechanism to the hydrogenolysis of cyclopentanes, which is in fact observed experimentally.

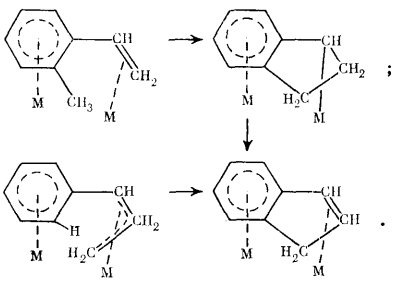
We may note that by no means all experimental data can be described in terms of the selective and non-selective mechanisms (or their linear combination). Maire et al.[62] were therefore forced to introduce the concept of the partially selective mechanism of hydrogenolysis, but it proved difficult to put forward any postulates concerning the character of the intermediate species. The results of a study[69] in which it was shown that the partially selective mechanism can be observed in those cases where the acid centres of the catalyst exhibit an appreciable activity in the hydrogenolysis of cyclopentanes are of interest in this connection. We may note that the interpretation of the results for the hydrogenolysis of alkylcyclopentanes must be treated with caution, since the monofunctional character of the catalysts employed has been no means always reliably demonstrated.

The C_5-Dehydrocyclisation of Alkanes

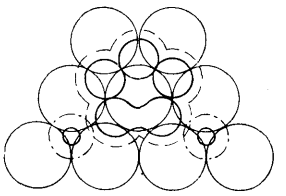
Data on the hydrogenolysis of alkylcyclopentanes in the presence of platinum catalysts suggested the following mechanism of the C_5-dehydrocyclisation of alkanes[45]:



An analogous mechanism has been proposed previously[70] for the C_5-dehydrocyclisation of alkylbenzenes in the presence of the Pt/Al_2O_3 and Pt/SiO_2 catalysts:



Other views concerning the structure of the transition state in the C_5-dehydrocyclisation of alkanes and the hydrogenolysis of cyclopentanes in the presence of Pt/C have been developed[54,59,71]. The hydrogenolysis of cyclopentane to pentane in the presence of this catalyst is known to proceed without the formation of side products at 200–290 °C. Neither n-pentane[71,72] nor cyclohexane[73] undergoes hydrogenolysis at these temperatures. These facts cannot be interpreted from the standpoint of the strain in the cyclopentane molecule[74] or the differences between the energies of the C–H and C–C bonds in these hydrocarbons[75]; however, they can be rationally accounted for within the framework of this sextet-doublet mechanism of the hydrogenolysis of cyclopentane hydrocarbons in the presence of the Pt/C catalyst, according to which[54,71] the carbon atoms of the five-membered rings are located in the interstices of the platinum (111) lattice on adsorption of the hydrocarbon. The geometrical requirements are such that one of the bonds in the ring is then extended, dissociating in the presence of adsorbed hydrogen. According to Liberman[54], the structure of the transition state can be represented schematically as follows:



where the large circles represent platinum atoms, the medium circles represent carbon atoms, and the small circles represent hydrogen atoms; the dashed lines denote the van der Waals volumes of the carbon and hydrogen atoms.

In conformity with the principle of microscopic reversibility, the C_5-dehydrocyclisation reaction of alkanes should proceed via the same transition state. According to this mechanism, an increase of the surface concentration of hydrogen should entail a decrease of the probability of the disposition of the substituents in the interstices of the platinum lattice following the adsorption of the cyclopentane hydrocarbon (which facilites the attack by hydrogen on the C–C bond adjoining the substituent), i.e. entails a decrease of the selectivity of the hydrogenolysis[59,76,77]. The increase of the fraction of 1,2-dimethylcyclopentane compared with ethylcyclopentane in the products of the C_5-dehydrocyclisation of n-heptane on passing from a flow to a pulsed system can be explained analogously[78]; here it is suggested that the lowest surface concentration of hydrogen is attained under the conditions of the flow system.

In the presence of rhodium, iridium, and osmium catalysts the hydrogenolysis takes place equally successfully for both cyclopentanes and for cyclohexanes and alkanes, which, together with certain other facts, led Bragin et al.[59] to the conclusion that the reaction proceeds via a doublet mechanism.

We may note that, although the models of the sextet-doublet and doublet mechanisms differ significantly in detail from the concepts of the selective and non-selective mechanisms of the hydrogenolysis of cyclopentanes, they also have certain features in common. In particular, in the hydrogenolysis via the non-selective mechanism[62] and the sextet-doublet mechanism, it is assumed that the ring of the molecule is arranged parallel to the surface of the metal. On the other hand, the question of the nature of the adsorption of the reacting molecule remains open within the framework of the sextet-doublet mechanism[54,71], although the authors have in fact indicated the possibility of physical adsorption.

Among other Group VIII metals, palladium[79,80], iridium[81,82], rhodium[83,84] and its alloys[85,86] exhibit a catalytic activity in the C_5-dehydrocyclisation of alkanes and their isomerisation via the C_5-ring mechanism.

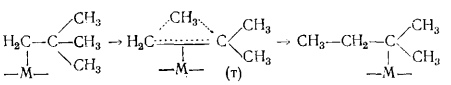
The characteristics and mechanisms of the isomerisation and cyclisation of aromatic alkyl-substituted hydrocarbons in the presence of platinum catalysts have been described in detail in recently published reviews[8,87].

III. THE MECHANISMS OF THE ISOMERISATION AND C_5-DEHYDROCYCLISATION REACTIONS OF ALKANES AND THE HYDROGENOLYSIS OF CYCLOPENTANES

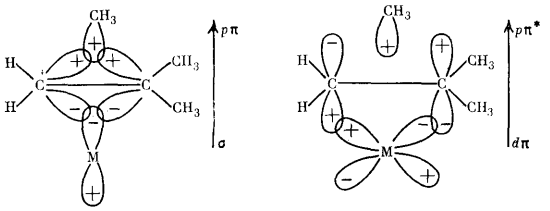
One of the fruitful methods for the investigation of reaction mechanisms involves the study of the reactions of model hydrocarbons (the term "model hydrocarbons" is treated here in a broad sense). With their aid, the investigator can make a choice between several alternative reaction mechanisms or can estimate the contributions of different mechanisms to the overall process. Hydrocarbons with a characteristic feature in the structure of the carbon skeleton, for example, the position of the substituents and the presence of a quaternary carbon atom or an isotope label, can be used as models. In most cases the difficulty of the synthesis of such hydrocarbons is compensated by the ease of the interpretation of the experimental data and the possibility of observing detailed features in the course of the reactions.

Thus the application of neopentane as a model hydrocarbon made it possible to introduce the concept of 1,3-diadsorption in isomerisation via the bond shift mechanism (the Anderson mechanism). Rooney and co-workers[88-90] demonstrated the ease of isomerisation on platinum (at 160–300 °C) and palladium (at 200–300 °C) of a series of polycyclic hydrocarbons for which the formation of 1,3-diadsorbed intermediate species is impossible or difficult. For example, the adsorption of the adamantane dimer during isomerisation then proceeds with elimination of only one hydrogen atom. This is also indicated by data for the D_2 exchange with this hydrocarbon.

In order to account for the characteristics of the isomerisation of polycyclic hydrocarbons, the following mechanism (henceforth referred to as the Rooney mechanism), considered for simplicity in relation to neopentane, has been suggested[90,91]:



In the transition state (T), the occupied $p\pi$ orbital of the hydrocarbon species overlaps with the σ orbital of the metal. Simultaneously the $d\pi$ orbital of the metal overlaps with the unoccupied antibonding $p\pi$ orbital of the hydrocarbon fragment:



The electron-deficient character of the $p\pi$ orbital explains some similarity of this mechanism with the carbonium ion mechanism of isomerisation. The character of the bonding in the transition state (T) resembles that in metal–olefin complexes. In conformity with this finding, platinum, which forms stronger metal–olefin bonds, is a better catalyst of isomerisation via the bond shift mechanism than palladium. Similarly, the greater selectivity of the (111) face of platinum compared with the other faces in isomerisation[53] cannot be explained by the more effective adsorption of the hydrocarbon on this face; the true explanation is that the (111) face has no affinity for the formation of a strong bond between the hydrocarbon and the surface, which is necessary for hydrogenolysis[6]. We may note that the transition state (T) cannot be common to the isomerisation and hydrogenolysis reactions of alkanes[91], in contrast to the Anderson mechanism according to which identical intermediate species are formed in these two reactions. We may draw attention to the similarity of the Rooney mechanism to the mechanism of the dehydroisomerisation of alkylcyclopentanes on platinum discussed above [see mechanism (1)].

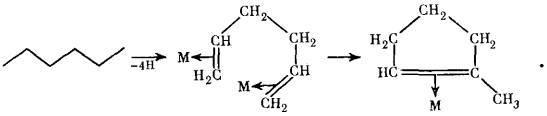
The isomerisation of neopentane on a platinum film in the presence of D_2 involves the formation of an appreciable amount of monodeuterated isopentane[92], which confirms, according to the authors, the formation of intermediate adsorbed alkyl species in the isomerisation reaction.

It was stated earlier that intermediate species of the type



may play an important role in the C_5-dehydrocyclisation and skeletal isomerisation of alkanes. This possibility is also confirmed by the results of the study of the C_5-dehydrocyclisation from the standpoint of the characteristics of electrocyclic reactions[93].

Comparative study of the reactions of a series of hexenes, hexadienes, hexa-1,3,5-triene, and n-hexane in a stream of hydrogen and helium on the Pt/Al_2O_3 catalyst[26] and in a mixture of these gases (20% H_2) on platinum black[24] showed that the yields of five-membered cyclic hydrocarbons are a maximum in the case of the initial hexa-1,5-diene. The amount of methylcyclopent-1-ene formed under these conditions increases with decrease of the dehydrogenating activity of the catalyst. The following cyclisation mechanism has been proposed on the basis of the facts presented above[94]:



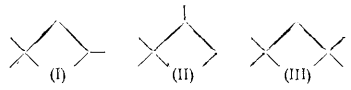
However, one should bear in mind that, together with processes involving the formation of a five-membered ring, other reactions proceed vigorously: skeletal isomerisation, double bond shift, aromatisation, dehydrogenation processes, and hydrocracking. Thus small changes in the yields of five-membered carbocyclic products may be associated, depending on the nature of the initial hydrocarbon, with a change in the contribution of different reactions to the overall process, particularly when the closure of the five-membered ring is the rate-limiting stage.

In order to investigate the role of olefins in the C_5-dehydrocyclisation reactions of alkanes, experiments were performed in which the alkane, alkene, and then again the alkane were passed over the Pt/C catalyst[27,95]. In the absence of a stream of H_2, different effects of the replacement of the initial hydrocarbon on the C_5- and C_6-dehydrocyclisations were demonstrated: in the latter case the introduction of an olefin into the reaction zone instead of the alkane increased the yield of the aromatic hydrocarbon, while the yield of alkylcyclopentanes fell. These facts indicate definite differences between C_5- and C_6-dehydrocyclisations; under the conditions investigated, the former proceeds in the presence of the Pt/C catalyst mainly via the direct pathway, bypassing the olefin-formation stage.

Under more severe conditions and in the presence of bifunctional catalysts[26,96-98], the reaction can also proceed differently, for example via two independent pathways: via the intermediate formation of olefins and via the direct closure of the five-membered ring. Quantitative data for these two pathways have been obtained by the kinetic isotope method[97,99];

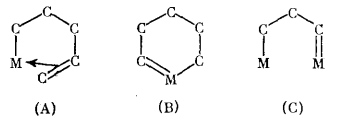
it was observed that the relative contributions of the two pathways vary with the experimental temperature and the nature of the catalyst. It is noteworthy that the rigorous application of the kinetic isotope method to the determination of the intermediates in the reaction is possible only in the presence of the adsorption–desorption equilibrium between the surface species and the corresponding compounds in the gas phase; however, this is not always achieved[25].

Another approach to the study of the possibility of the intermediate formation of π-adsorbed α-olefins in the C_5-DHC of alkanes has been used[100]: the reactions of 2,2,4-tri-methylpentane (I), 2,2,3-trimethylpentanes (II), and 2,2,4,4-tetramethylpentanes (III) on platinum and palladium films were investigated:

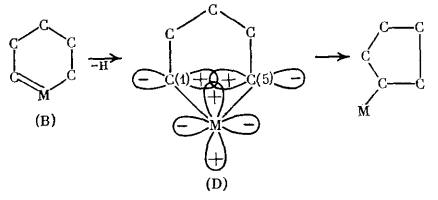


On platinum, the C_5-dehydrocyclisation of these hydrocarbons is the main process, the ratios of the rates of cyclisation of compounds (I), (II), and (III), being 1.2:1.2:1.0. In the presence of palladium, compound (II) cyclises at a rate higher by an order of magnitude than compound (I) and higher by two orders of magnitude than compound (III), the C_5-dehydrocyclisation of these hydrocarbons not being the main process. In an earlier study[111] similar results were obtained in the presence of the 20% Pt/C catalyst: under the same conditions, the yields of the cyclic products were 14% from compound (I) and 21% from compound (III). However, no conclusions about the reaction mechanism were reached[101].

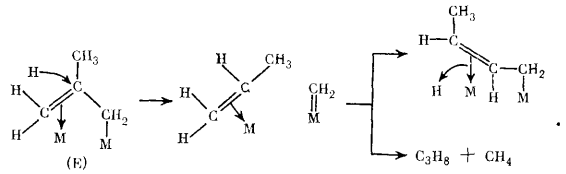
The results of Muller and Gault[100] suggested that the cyclisation on platinum takes place via the intermediate formation of the species (B) but not (A), while on palladium the species (A) cyclise:



Cyclisation via the (B) stage can proceed as a result of simple *cis*-ligand inclusion; this results in the formation of adsorbed cyclopentane. An alternative pathway (possibly more favourable) involves the formation of the (D) state in which the 2*p* orbitals of the C(1) and C(5) atoms and the *d* orbital of the metal atom form an occupied bonding molecular orbital, two unoccupied non-bonding orbitals, and an antibonding orbital:

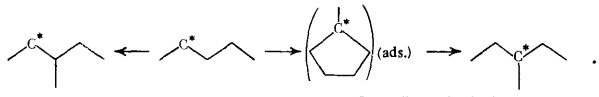


This mechanism of cyclisation on platinum [via the formation of the (B) or (D) state] is analogous to the mechanism of the skeletal isomerisation via bond shift with the intermediate formation of (C). Intermediates of type (C) do not account for the characteristics of the isomerisation on palladium. In the latter case the following mechanism of isomerisation and hydrogenolysis with participation of adsorbed hydrogen has been suggested[100]:



The necessity for the formation of an intermediate of type (E) explains the difficulty of isomerisation on palladium with participation of a quaternary atom. Thus the expansion of the ring of 1,1,3-trimethylcyclopentane on palladium proceeds via a tertiary carbon atom, while on platinum the expansion involves a quaternary carbon atom[13]. Neopentane readily isomerises on platinum, while on palladium the reaction does not occur under the usual conditions[47].

The use of mass spectrometry to determine the position of ^{13}C in labelled hydrocarbons[15] made it possible to use the latter to investigate the mechanisms of catalytic reactions. Thus in the case of the ^{13}C-labelled 2-methylpentane it is possible to distinguish the bond shift and C_5-cyclic isomerisation mechanisms:



The reactions of isomeric hexanes labelled with ^{13}C have been studied in the presence of the 0.2% Pt/Al_2O_3 [102] and 10% Pt/Al_2O_3 [103] catalysts and also on a platinum film [104] in a stream of hydrogen. The distribution of the label in the products shows that the isomerisation in the presence of the Pt/Al_2O_3 catalyst containing 0.2% Pt proceeds mainly via the C_5-cyclic mechanism; in the presence of Pt/Al_2O_3 with a 10% content of platinum and on a platinum film, the bond shift mechanism makes a significant contribution to the isomerisation process. It was found that in the adsorbed phase several consecutive rearrangements can occur in the molecule, their number being greater in the presence of the 10% Pt/Al_2O_3 catalyst and a platinum film than in the presence of the 0.2% Pt/Al_2O_3 catalyst. Not only the content (and the degree of dispersion) of the platinum in the catalyst, but apparently also the partial pressure of hydrogen influence the number of rearrangements in the adsorbed phase under these conditions, but the authors did not investigate the influence of this factor. Unfortunately, no data are quoted[102,103] concerning the hydrogen/hydrocarbon ratio; the conclusion that the ratio was small in the above studies[103,104] can be reached only on the basis of later investigations, for example, that of Garin and Gault[105].

The examples examined above demonstrate the great effectiveness of the study of the reactions of model hydrocarbons whose geometry permits a choice between the possible reaction mechanisms. However, the extension of certain conclusions to a wider range of starting materials always requires some caution, because one cannot rule out the possibility that the molecular geometry (for example, stereochemical limitations) actually prevents the occurrence of the reaction via an alternative pathway. When geometrical limitations are removed, such a pathway may become entirely possible. The application of labelled compounds, which permit the determination of the relative contributions of different reaction pathways without influencing the course of the reaction, is promising from this standpoint. In a number of instances the study of the position of the ^{13}C label in the reaction product makes it possible to determine the rate-limiting stage of the reaction.

IV. THE INFLUENCE OF HYDROGEN ON THE DEHYDROCYCLISATION AND ISOMERISATION REACTIONS OF ALKANES. KINETIC STUDIES

The role of hydrogen in the hydrogenolysis of alkylcyclopentanes and the dehydrocyclisation and skeletal isomerisation of alkanes was elucidated both in independent studies and within the framework of kinetic investigations. Whereas hydrogen is a direct participant in the first of the above reactions, in C_5-dehydrocyclisation and skeletal isomerisation it is involved as an astoichiometric component[106]. The study of the role of hydrogen in these reactions made it possible to discover certain additional details of their mechanisms.

A characteristic feature of the influence of hydrogen on the catalytic reactions of hydrocarbons in the presence of platinum catalysts is the presence of a maximum on the plot of the reaction rate (the yield of reaction products) against the partial pressure of hydrogen when p_{H_2} is varied within fairly broad limits. Such relations have been observed for the dehydrocyclisation and skeletal isomerisation of C_6-hydrocarbons on platinum black[107-112], in the presence of the Pt/C catalyst[113] and bifunctional Pt/Al_2O_3 and $Pt-Re/Al_2O_3-F$ catalysts[114] for the dehydroisomerisation of methylcyclopentane[41], the skeletal isomerisation of n-heptane[115] and certain C_4-C_6 alkanes[116-118], and for the dehydrocyclisation of n-heptane[119] in the presence of bifunctional platinum/alumina catalysts.

The position of the maximum depends in the general case on the experimental conditions: on the catalysts employed, on the type of reaction considered, on the structure of the initial hydrocarbon, on the experimental temperature, etc. As an example, we shall consider the results of our investigations[113,114,120] in which the influence of the concentration of hydrogen on the C_5-DHC and the skeletal isomerisation of alkanes and alkenes was studied on deposited platinum catalysts of different types—platinised charcoal and bifunctional platinum/alumina and platinum–rhenium/alumina catalysts. The positions of the maximum are different on plots of the yield of C_5-DHC products and the products of the skeletal isomerisation of alkanes against the partial pressure of hydrogen. In the case of C_5-DHC the coordinates of the maximum depend little on the reaction temperature and the structure of the initial alkane. The optimum H_2 concentration for the skeletal isomerisation of alkanes depends on their structure: for a more branched hydrocarbon, the maximum lies at higher H_2 concentrations. A decrease of temperature shifts the position of the maximum towards lower H_2 concentrations, which indicates the important role of the surface hydrogen in the skeletal isomerisation reaction (the concentration of such hydrogen increases with decrease of temperature). We may note the similarity of the relations obtained in the reactions of 3-methylpentane and 3-methylpent-2-ene in the presence of the Pt/C catalyst. This shows that the formation of methylcyclopentane from an alkane and alkene in the presence of H_2 apparently proceeds via similar intermediate stages.

We may note that the five-membered carbocyclic products derived from both alkanes and olefins and dienes are formed only in the presence of hydrogen[94,107,108]. In the presence of platinum black the skeletal isomerisation of alkanes in H_2 proceeds via both the C_5-cyclic mechanism and the bond shift mechanism. In the absence of hydrogen the isomerisation can take place only via the bond shift mechanism[109]; the C_6-DHC reaction of n-hexane on platinum black[107] and in the presence of the Pt/Al_2O_3 catalyst[79] takes place at an appreciable rate also in a stream of helium, in contrast to C_5-DHC. However, it has been stated[119] that under reforming conditions the rate of aromatisation of n-heptane on the Pt/Al_2O_3 catalyst is virtually zero in the absence of hydrogen.

Comparative study of the influence of the partial pressure of hydrogen on the C_5-cyclisation and skeletal isomerisation of 3-methylpentane and 3-methylpentenes on platinum black enabled Paal et al.[121] to postulate the operation of two different mechanisms of the formation of the C_5 ring. According to the authors[121], at a low hydrogen concentration the cyclisation proceeds via the intermediate formation of highly dehydrogenated species (for example, of the alkenyl type). At higher pressures, the cyclisation takes place via a "two-centre" mechanism involving the intermediate formation of semihydrogenated products, which are apparently "weakly" adsorbed on platinum centres, while the new C–C bond is formed as a result of the interaction of the terminal atoms of the carbon chain with other platinum centres. The operation of the "two-centre" mechanism of the C_5-dehydrocyclisation may be indicated by the following facts: the similarity of the nature of the reaction of 3-methylpentane and 3-methylpentenes under these conditions (there are no differences between the reactivities of *cis*- and *trans*-3-methylpent-2-enes), the proportionality of the rate of cyclisation and the hydrogenating activity of the catalyst[121], and data for the deactivation of platinum black under the influence of the hydrocarbon[122].

An attempt has been made[111] to describe the kinetics of the isomerisation of 3-methylpentane on platinum black in a static system. The kinetic equation obtained for the "two-centre" mechanism of isomerisation describes satisfactorily the character of the influence of hydrogen on the rate of reaction in qualitative terms, but the authors[111] did not provide a complete multistage scheme for the reaction and did not carry out a mathematical treatment of the experimental results.

The data examined show that hydrogen exerts a promoting or inhibiting influence on the reactions of hydrocarbons depending on the experimental conditions and the catalyst. This is associated with various functions performed by hydrogen on the surfaces of metallic catalysts. We may note the most important of these, which are discussed in the communications quoted above.

Vigorous dehydrogenation processes, leading to the formation of strongly adsorbed hydrocarbon fragments on the surface, take place at low H_2 pressures in the presence of platinum catalysts. By suppressing the above process, hydrogen increases the working area of the catalyst, which accelerates the reactions. On the other hand, hydrogen promotes the desorption displacement of the products of the reactions of hydrocarbons.

At fairly high partial pressures of hydrogen, the chemisorption of the hydrocarbon is suppressed as a consequence of the competitive character of the adsorption of hydrogen and the hydrocarbon. Hydrogen also prevents the dissociation of the initial hydrocarbon on the surface, which inhibits the reactions. Overall, when p_{H_2} is varied widely, the causes considered here lead to the appearance of maxima on the curve relating the yields of the reaction products to p_{H_2}.

One cannot rule out the possibility that, for different degrees of coverage of the catalyst surface with hydrogen, the rate-limiting state and the reaction mechanism can be different. Thus, according to our data[113], the skeletal isomerisation in the presence of the Pt/C catalyst proceeds via the C_5-cyclic mechanism over the entire range of hydrogen concentrations investigated. In the presence of bifunctional catalysts[114], the relative contributions of different mechanisms depend on the partial pressure of hydrogen and the acidity of the catalyst. At high partial pressures of

hydrogen the C_5-cyclic mechanism of isomerisation predominates and at comparatively low partial pressures another pathway, apparently involving the acid centres of the catalyst, makes a significant contribution.

The possibility of the involvement of hydrogen as an astoichiometric component in the reactions of hydrocarbons is of fundamental importance. Its role may not reduce solely to influencing the adsorption-desorption stages. It has been suggested[96,98] that hydrogen not only promotes the removal of the strongly adsorbed carbon-containing species but is also directly involved in the C_5-dehydrocyclisation reaction of alkanes itself. In our studies these views were further developed[113,114,120,123].

New data concerning the role of hydrogen in the C_5-DHC reaction of alkanes in the presence of the Pt/C catalyst have been obtained[120,123] in a study of the kinetics of the C_5-DHC of iso-octane. It was shown that, in the range of partial pressures of the reactants investigated, the C_5-DHC reaction is accelerated by hydrogen and inhibited by 1,1,3-trimethylcyclopentane. We put forward the following kinetic equation:

$$r = (kp_A - k'p_Bp_H)\Big/\left[\frac{p_A}{p_H^{0.5}} + A_1\frac{p_B}{p_H^{0.5}} + A_2p_H^{0.5} + A_3p_A\left(\frac{A_4}{p_H}\right)^{0.5(n+1)}\right],$$

where r is the rate of reaction, p_A, p_B, and p_H are the current partial pressures of iso-octane, 1,1,3-trimethylcyclopentane, and hydrogen respectively, and k, k', A_1, A_2, A_3, and n are constants whose physical significance is discussed by Krasavin et al.[123] Analysis of this equation using the numerical values of the constants indicated by Krasavin et al.[123] makes it possible to predict the appearance of a maximum on the curve relating the reaction rate to the partial pressure of hydrogen when p_{H_2} is varied widely. The position of the maximum depends on the stability of the surface carbon-containing compounds: with its increase, the maximum shifts towards higher values of p_{H_2}.

An important factor, observed by the present authors[120], is the occurrence of a kinetic isotope effect in the C_5-DHC reaction of iso-octane in the presence of a Pt/C catalyst when hydrogen is replaced by deuterium. The kinetic isotope effect $r_H/r_D = 2$ indicates the involvement of hydrogen in the slow stages of the C_5-DHC reaction. Under the same conditions, the rate of exchange of deuterium for hydrogen in iso-octane greatly exceeded the rate of the C_5-DHC reaction. This shows that the adsorption stage must apparently be regarded as rapid. The set of data obtained enabled us to describe the C_5-DHC reaction in terms of the following multistage scheme[123]:

(1) $H_2 + 2Z \rightarrow 2HZ$,

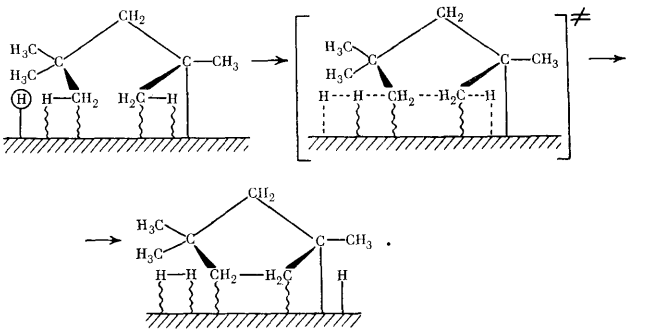
(2) $C_8H_{18} + HZ \rightarrow C_8H_{17}Z + HZ \rightarrow C_8H_{17}Z + H_2$,

(3) $C_8H_{17}Z + nHZ \rightarrow C_8H_{17-n}Z + nH_2 + nZ$,

(4) $C_8H_{17}Z + HZ \rightarrow$ (cyclo-C_8H_{15})$Z + HZ + H_2$,

(5) (cyclo-C_8H_{15})$Z + H_2 \rightarrow$ cyclo-$C_8H_{16} + HZ$.

Here Z denotes a site on the surface of platinum. Dissociative adsorption of the initial hydrocarbon when the latter interacts with surface hydrogen with simultaneous evolution of molecular hydrogen is postulated in stage (2). The $C_8H_{17}Z$ fragment formed can undergo further dissociation (stage 3). This pathway apparently does not lead to the formation of the C_5-DHC products under the conditions investigated, but stage (3) explains the multiple exchange of deuterium for hydrogen in the higher alkanes and certain characteristic features of the behaviour of the Pt/C catalyst at $p_{H_2} < 0.4$ atm. Stage (4) describes the cyclisation of the $C_8H_{17}Z$ fragment. The formation of the C_5 ring on the surface can be represented as follows:



Here the continuous lines denote the chemisorption linkages with the surface, the wavy lines indicate the topography of the disposition of the atoms at the surface, and the dashed lines represent the redistribution of bonds in the associative transition state.

Thus the hydrogen chemisorbed on the catalyst reacts with the $C_8H_{17}Z$ surface fragment to form a transition state in which the loosening of the H–C bond is accompanied by the simultaneous formation of a C–C bond in the hydrocarbon under the influence of the activated hydrogen species (the latter is enclosed in a circle). The surface cyclic compound formed reacts with molecular hydrogen in stage (5) of the mechanism under consideration to form the final reaction product and adsorbed hydrogen. According to the views developed here, adsorption and cyclisation takes place at different fairly close centres on the catalyst surface.

In the experimental temperature range (280–325 °C) stage (1) is rapid. Stages (2) and (3) can also be regarded as rapid, since the rate of isotope exchange between deuterium and the hydrocarbon is much higher than the rate of the C_5-DHC reaction. Stage (5) should likewise be regarded as rapid, since otherwise it would be impossible to explain the observed inhibition of the reaction by its product. It remains to assume that the slow stage in the above mechanism is stage (4), which agrees with the acceleration of the reaction when the hydrogen concentration is increased and with the presence of the kinetic isotope effect on replacement of H_2 by D_2.

Thus the results of the study of the influence of hydrogen on the C_5-DHC reaction of alkanes can be interpreted on the basis of the multistage scheme considered and the equation presented above. Other possible C_5-DHC mechanisms proposed in the literature are in poorer agreement with experimental data. However, we may note that, when the C_5-DHC reaction is carried out under other conditions (for example, in the presence of highly dispersed catalysts at higher temperatures or in the presence of a deficiency of hydrogen), the mechanism as a whole can change. On the basis of the above scheme, it is easy to set up a multistage scheme for the skeletal isomerisation of alkanes via the C_5-cyclic mechanism and to derive a kinetic equation which, as for the C_5-DHC reaction of alkanes, makes it possible to interpret the appearance of maxima on the curves relating the yields of skeletal isomers to the partial pressure of hydrogen.

It was shown previously[124,125] that the activation energy for the C_5-DHC of alkanes on platinised charcoal is almost independent of the structure of the hydrocarbon and amounts to 83.7 kJ mol^{-1} (the data were obtained under the conditions

of a zero-order reaction). For alkylbenzenes, this quantity increases by 31.4 kJ mol^{-1}.

Negative formal reaction orders with respect to hydrogen as well as apparent activation energies have been found for the isomerisation of n-butane and isobutane on platinum black[126] (the activation energies are respectively 100 and 121 kJ mol^{-1}).

Few kinetic studies have been made on the isomerisation of alkanes; most of them[116–118,127–131] were carried out in the presence of industrial platinum/alumina bifunctional reforming catalysts. In the analysis of the kinetics, the slow stage is usually assumed to be that involving the isomerisation on the acid centres of the catalyst; the kinetic equations are characterised by negative or zero reaction orders with respect to hydrogen. Account has also been taken[128] of the influence of the poisoning of the catalyst by coke on the rate of isomerisation.

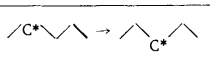
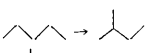
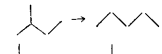
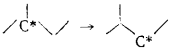
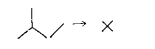
In a study of the isomerisation of pentane in the presence of a platinum/alumina catalyst by the flow-circulation method, the reverse kinetic isotope effect was observed[130,131] on replacement of hydrogen by deuterium. The rate of reaction was characterised by a positive order with respect to hydrogen, equal to 0.5, and the rate of exchange of deuterium in pentane under these conditions was higher than the rate of isomerisation. The above facts suggested that hydrogen is involved in the slow stage of the reaction—the isomerisation of the adsorbed fragment on the acid centres of the catalyst.

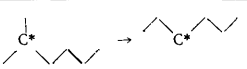
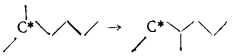
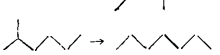
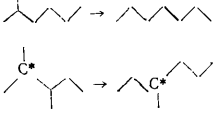
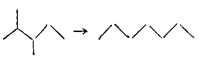
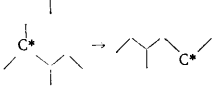
Interesting studies on the isomerisation reaction, particularly the C_5-DHC of alkanes in the presence of platinum/alumina catalysts under the conditions of monofunctional catalysis, have been carried out in recent years by Gault and co-workers[132]. We may note the fruitfulness of the approach by the authors, which combines kinetic studies with the employment of the method of labelled (^{13}C) molecules for reactions of the groups of C_5–C_7 alkanes in the presence of platinum catalysts with different degrees of dispersion. Since the change in the position of the ^{13}C label in the isomerisation products could always be predicted as a result of only one rearrangement (via the C_5-cyclic mechanism or the bond shift mechanism) of the adsorbed fragment on the surface, it was suggested that the rate-limiting stage is skeletal rearrangement on the catalyst surface, while the adsorption–desorption stages are fast. The Table presents the apparent activation energies and the formal reaction orders with respect to hydrogen according to the results of Garin and Gault[105]. For C_6 alkanes, it has only been stated that the orders of the isomerisation reaction with respect to hydrogen are negative[132].

According to the analysis by Sinfelt[133], a negative reaction order *b* with respect to hydrogen implies that the initial hydrocarbon is adsorbed dissociatively with abstraction of at least 2*b* hydrogen atoms. In order to account for the high negative orders of the pentane isomerisation reaction with respect to hydrogen (see Table), it is necessary to postulate extensive dehydrogenation of the initial hydrocarbon molecule, which appears unlikely under the conditions of an excess of hydrogen. On this basis, preference was given[105,134] to the so-called reaction mechanism in which the Frennet adsorption model[135,136] is used. The competative adsorption of hydrogen and the alkane on the same active centres of the catalyst is considered within the framework of this model, hydrogen occupying one such surface centre and the hydrocarbon a group (ensemble) of several centres.

It has been shown[105] that, in the dissociation of an alkane via the "bimolecular reaction" mechanism, the order of the reaction *b* with respect to hydrogen corresponds to the abstraction of only *b* hydrogen atoms; in addition, comparatively simple explanations have been found for the positive reaction order with respect to hydrogen in the isomerisation of C_7 alkanes and also for the characteristic features of the variation of the selectivity of the isomerisation reaction with the H_2 concentration in the system. Overall, the employment of the Frennet model for the interpretation of kinetic data appears to us extremely fruitful, but a quantitative test of the kinetic equations obtained on the basis of the "bimolecular reaction" is difficult because it requires the knowledge of the alkane adsorption isotherm in the presence of hydrogen, which is itself a fairly difficult experimental problem.

The activation energies (kJ mol^{-1}) and the kinetic orders with respect to hydrogen (*b*) of the isomerisation reactions of various C_5 and C_7 alkanes in the presence of a platinum/alumina catalyst (according to the data of Garin and Gault[105]).

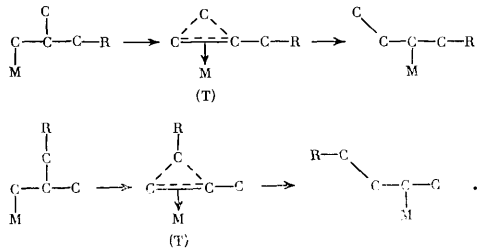
No.	Reaction	E_a	*b*
1		297.3±6.3	−3.4
2		231.5±6.3	−1.8
3		244.3±6.3	−2.3
4		189.7	−1.9
5		188.4	−1.65

No.	Reaction	*b*
6		0.9±0.2
7		1.8±0.2
8		0.2±0.2
9		0.8±0.1
10		1.4±0.1
11		0.7±0.1

Note. The molecular skeleton and the position of the ^{13}C label are indicated. Reactions (1), (6), (9) and (10) have the C_5-cyclic mechanism, while others proceed via the bond shift mechanism.

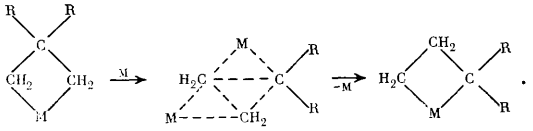
On the basis of kinetic data (see Table), it has been suggested[132] that isomerisation reactions involving the bond shift mechanism be divided into two groups: the "chain elongation" reaction (for example, the isomerisation of isopentane to pentane and conversely) and the "methyl shift" reaction. They have different activation energies and formal orders with respect to hydrogen and also exhibit variations,

characteristic of each group, of the relative rates of isomerisation via different pathways with the structure of the initial hydrocarbon for reactions of the homologues of C_5–C_7 alkanes (the so-called structural effect).[134,137,138]. It has been suggested that the mechanisms of these two isomerisation reactions are different. The characteristic features of the "chain elongation" reaction are best described by the Rooney mechanism:

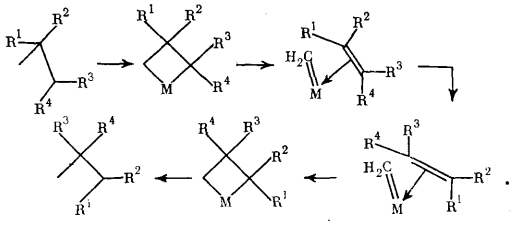


Thus, from an analysis of the stabilisation of the transition state (T), it proved possible[137] to explain the character of the variation of the relative contributions of the above reaction pathways in the isomerisation of alkanes with different alkyl substituents.

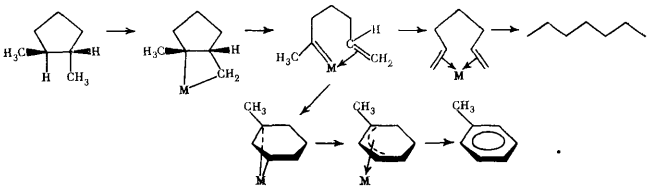
In order to account for the characteristic features of the "methyl (alkyl) shift" reaction, two new mechanisms were proposed, since the bond shift isomerisation mechanisms considered previously did not explain the entre set of data obtained[138,139]. In an earlier study[105] it was postulated that the isomerisation proceeds via the formation of intermediate methylcyclobutane species and a quasicyclopropane intermediate, arranged in a virtually flat position on the catalyst surface:



An alternative concept is in better agreement with the chemistry of coordination compounds and consists in the reversible dismutation of methylcyclobutane to a metallocarbene and a π-adsorbed olefin[138,139]:

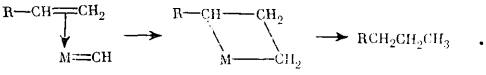


A characteristic feature of this mechanism is that its occurrence requires the free rotation of the olefin about the bond with the metal. The introduction of bulky alkyl substituents hinders the rotation; this made it possible to explain the differences between the rates of isomerisation of different labelled [^{13}C] heptanes. It has been suggested that the cyclopentane ring can also undergo hydrogenolysis via an analogous mechanism[139]—one of the variants of the partly selective mechanism of hydrogenolysis:



This mechanism explained certain features of the hydrogenolysis of 1,2-dimethylcyclopentane and also the C_5- and C_6-DHC of labelled [^{13}C] heptanes[138,139].

Although the methylcyclobutane mechanism provides a satisfactory explanation of the fundamental features of the hydrogenolysis of alkanes, it was recently criticised from an unexpected direction. Clarke, Rooney, and co-workers[86,140] observed the conversion of alkanes into higher homologues on films of different metals (W, Pd, Pt, Rh, Ru, Nb, Mo) and obtained evidence for the following mechanism:



(it is the reverse of the mechanism of the hydrogenolysis of alkanes examined above). It was found that platinum is relatively inactive in the homologue generating reaction although it is one of the active metals in the isomerisation of hydrocarbons via the bond shift mechanism. On the other hand, tungsten is relatively inactive in isomerisation and is the most active among the metals investigated in the formation of higher homologues of alkanes. This shows that the mechanism of isomerisation via the reversible dismutation of a metallocarbene and an olefin is not important in the presence of platinum catalysts. It is believed[86,140] that the principal mechanism of the bond shift isomerisation in the presence of platinum is that of Rooney, i.e. the reaction proceeds via the formation of adsorbed species analogous to non-classical carbonium ions. A mechanism involving α,ε-diadsorbed species has also been proposed for C_5-DHC.

The mechanisms of the isomerisation of alkanes in the presence of other Group VIII metals have been investigated significantly less thoroughly than the mechanisms of reactions in the presence of platinum catalysts. In many instances the study of the characteristic features of the isomerisation suggested new isomerisation mechanisms. Thus a concerted mechanism via the formation of a quasi-cyclobutane intermediate (the 1–3-ethyl shift mechanism) has been postulated for the isomerisation of methylpentanes in the presence of the Ir/Al_2O_3 catalyst[141].

V. THE INFLUENCE OF THE STRUCTURE OF METALLIC CATALYSTS ON THE MECHANISMS OF THE DEHYDROCYCLISATION AND SKELETAL ISOMERISATION REACTIONS OF ALKANES

The structure of metallic catalysts (the concentration and degree of dispersion of the metal, the orientation of the crystal faces, and the nature of the carrier) influence significantly the character of the processes occurring. Thus in a series of studies[142–146] of the kinetics of various reactions in the presence of metal single crystals with simultaneous determination of the structure and composition of the surface by low energy electron diffraction and Auger spectroscopy, it was shown that the rates and selectivities of many reactions depend on the structure of the platinum single crystal face. For example, the stepped faces are the most active in the dehydrocyclisation of n-heptane to toluene. The important

role of the formation of a new phase (a carbon-containing layer) on the catalyst surface in the reaction was noted. The ordered carbon-containing layer formed on the stepped faces has little influence on the dehydrocyclisation of n-heptane. On smooth faces a disordered layer is formed, which is one of the causes of the rapid loss of activity by the catalyst[146].

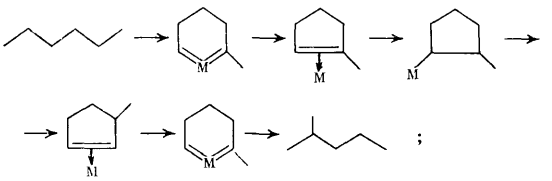
The question of the dependence of the selectivity of the hydrogenolysis of methylcyclopentane and the isomerisation of hexanes on the degree of dispersion of the catalyst was discussed vigorously in earlier studies. Whereas the influence of the degree of dispersion of the deposited metal on the selectivity of these reactions has been demonstrated in a number of studies[45,62,147,148], the data of Dautzenberg and Platteeuw[14,149] indicate the independence of the selectivity of the reactions on the size of the platinum crystals (when the latter is varied in the range 15–80 Å). Without dwelling in detail on this controversy, we should like to draw attention to the conclusion[150] that the ratios of the numbers of different centres are determined by the size of the crystallites in the early stages of the reduction of the catalyst. This conclusion is confirmed by the fact that sintering of identically reduced catalysts does not alter the selectivity of the hydrogenolysis of methylcyclopentane with increase in the size of the platinum crystallites[103]. From this conclusion, certain differences between the results obtained by the two groups of investigators mentioned above can be explained by the significant difference between the reduction temperatures of the catalysts which they employed. On the whole, one may regard it as established that the non-selective C_5-cyclic mechanism of isomerisation and hydrogenolysis predominates in the presence of highly-dispersed platinum catalysts reduced under mild conditions. In the presence of a catalyst with a low degree of dispersion, the hydrogenolysis of the C_5 ring becomes selective and the isomerisation of alkanes takes place to a significant extent via the bond shift mechanism[102,103,151,152].

More detailed studies in the presence of a series of platinum/alumina catalysts with different degrees of dispersion showed[153–155] that the overall rates of isomerisation of hexanes and of the hydrogenolysis of methylcyclopentane are independent of the degree of dispersion, i.e. these reactions are structure-insensitive as regards rate, but are structure-sensitive as regards selectivity. The following features were discovered. In the reaction 2-methylpentane → 3-methylpentane the relative contributions of the C_5-cyclic and bond shift mechanisms remain constant over a fairly wide range of crystallite dimensions. However, the character of the hydrogenolysis of the C_5 ring varies continuously from selective to non-selective with decrease in the size of the crystallites.

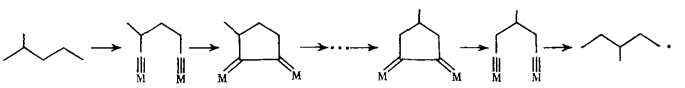
As the size of the crystallites falls below 20 Å, sharp changes take place in the character of the reaction. In the presence of such catalysts, the selectivity of the isomerisation of neopentane with respect to its hydrogenolysis diminishes significantly[156]. The mechanism of the hydrogenolysis of the five-membered ring becomes fully non-selective[153–155]. On very small particles (less than 10 Å), the isomerisation of hexanes via the bond shift mechanism hardly occurs. Somewhat different data were obtained in a study[157] where the sensitivity of the isomerisation reaction of n-hexane to structure is attributed solely to particles with dimensions less than 20 Å, while on larger platinum crystallites the reaction is structure-insensitive.

The characteristic features of the influence of the size of crystallites on the mechanism of the hydrogenolysis of alkylcyclopentanes justified the following schemes for isomerisation via the C_5-cyclic mechanism with participation on metallocarbenes and metallodicarbynes as intermediates[132,155]:

(1) the non-selective mechanism



(2) the selective mechanism



The additional hypothesis that both mechanisms involve a common intermediate, namely an α-adsorbed olefin which is then converted into a metallocarbene or a metallodicarbyne, has been put forward[138]. Although this hypothesis explained the proportions of the products of the C_5-DHC of 3-methylhexane, it made it difficult to interpret data[100] showing the equality of the rates of cyclisation of 2,2,4-tri-, 2,2,2-tri-, and 2,2,4,4-tetra-methylpentanes in the presence of platinum.

We may note that neither the metallocarbene nor the metallodicarbyne mechanism of the hydrogenolysis of alkylcyclopentanes explains the hydrogenolysis of the quaternary-secondary C–C bonds in the cyclopentane ring. However, it has been shown recently[158] that the quaternary-secondary C–C bond in *gem*-dimethylcyclopentane can be cleaved in the presence of the Pt/C catalyst.

The operation of the selective mechanism of the hydrogenolysis of cyclopentanes (and hence of the isomerisation of alkanes) in accordance with the schemes examined above, requires a larger ensemble of platinum atoms than for the non-selective mechanism and the relative contributions of these two mechanisms must therefore be influenced by the geometrical factor. If it is supposed that only the edge atoms of the platinum crystallites promote the formation of reactive species, then the critical size of the crystallite required for the transition from one mechanism to another must be approximately 25 Å. This is the minimum dimension for a crystallite which has two neighbouring edge (but not corner) platinum atoms[132].

The decrease of the selectivity of the isomerisation of neopentane in the presence of highly dispersed catalysts is attributed analogously[156] to the transition from the many-centre bond shift mechanism (via the formation of 1,1,3-adsorbed species) to the one-centre isomerisation mechanism (the Rooney mechanism), which, however, is characterised by a lower rate.

It has been suggested that the relative contributions of the C_5-cyclic and bond shift isomerisation mechanisms depend primarily on electronic factors[155], which may be significant for crystallites whose size is less than 10–15 Å[159] (the second critical size of crystallites). Thus the two critical dimensions of crystallites in the reactions involving the isomerisation of alkanes and the hydrogenolysis of cyclopentanes are a consequence of the operation of geometrical and electronic factors[132].

Certain additional evidence for the influence of the electronic and geometrical factors on the isomerisation mechanism can be obtained from a comparison[132] of the catalytic effects of different metals with the same degrees of dispersion (particle size 80 Å). Thus the isomerisation in the presence of the Ir/Al_2O_3 catalyst takes place only via the selective C_5-cyclic mechanism[82], in the presence of the Pd/Al_2O_3 catalyst the reaction involves the non-selective C_5-cyclic mechanism with a small contribution by the bond shift mechanism[160], while in the presence of the Pt/Al_2O_3

catalyst the reaction proceeds mainly via the bond shift mechanism with participation of both C_5-cyclic isomerisation mechanisms. However, one should note that the comparison of the catalytic activities of the above catalysts cannot be regarded as sufficiently rigorous: the published data for the reaction mechanisms refer to different temperatures (the reaction temperature can influence the process selectivity).

Certain features of the structure sensitivity of the alkane isomerisation reaction suggested[154] the possibility of the migration of the reactive adsorbed species from the adsorption–desorption centres to the reaction centres and conversely. Thus the overall isomerisation mechanism includes the stages involving the adsorption of an alkane molecule from the gas phase on a crystal face of platinum with formation of a weakly adsorbed species, surface migration from the adsorption centre to the reaction centre located on the surface of the metallic particle, the formation of highly dehydrogenated species on the reacton centre, their skeletal rearrangement and subsequent rehydrogenation, and surface diffusion and desorption of the reaction products. Analysis of the relative rates of different stages in the above mechanisms as well as the number of active centres led to a classification of the reactions in terms of their structure sensitivity. However, within the framework of the above study[154], one cannot assume that the surface diffusion of carbon-containing species has been proved. On the other hand, in the presence of an excess of hydrogen the formation of highly dehydrogenated species of the type of metallocarbenes and metallodicarbynes appears unlikely. This confirms indirectly the results of a study[140] in which it was shown that platinum is relatively inactive in the formation of carbene species.

One must not fail to mention, at least briefly, yet another promising method for the elucidation of the mechanisms of catalytic reactions in the presence of platinum catalysts—by the study of the reactions of hydrocarbons in the presence of alloys of platinum with Group IB metals, for example, gold or copper (the latter are virtually inactive in the reactions considered). A change in the platinum concentration in the alloy can alter the size of the platinum ensembles and also their electronic properties. It is difficult to separate the geometrical and electronic factors (it is probably actually impossible to do this); however, in many studies only the influence of the geometrical factor has been considered as the alloy composition was varied.

The study of the reactions of hydrocarbons in the presence of deposited Pt–Au and Pt–Cu alloys[161–165] permitted the following conclusions. At a high platinum concentration in the alloy the reactions proceed mainly via many-centre mechanisms: the selective C_5-cyclic mechanism of isomerisation and C_5 ring closure and opening and the bond shift mechanism involving the intermediate formation of, for example, 1,1,3-adsorbed species. A decrease of the concentration of platinum in the alloy suppresses the many-centre isomerisation mechanisms as a consequence of which the reaction proceeds via the non-selective C_5-cyclic mechanism with a small contribution to the isomerisation by the one-centre bond shift mechanism (the Rooney mechanism). The nature of the reactions of hydrocarbons in the presence of alloys with a low platinum content is analogous to the characteristic features of the reactions in the presence of highly dispersed platinum catalysts. On highly dilute alloys (with a platinum concentration of several per cent), the isomerisation of alkanes proceeds only via the one-centre bond shift mechanism. Certain characteristics of the reactions in the presence of platinum alloys have been explained[165] by the influence of the nature of the carrier and heat treatment temperature on the degree of carbidisation of the alloy surface or on the topography of the surface. It has been suggested in all cases that the isomerisation via the many-centre mechanisms is faster than via the one-centre mechanisms.

In many instances there are discrepancies between the experimental data obtained by different groups of investigators[164,165]. The characteristic features of the catalytic activity of alloys probably require further study. The importance of the investigation of reactions on alloys is also confirmed by the fact that the possibility of the C_5-DHC of alkanes in the presence of rhodium catalysts was demonstrated for the first time precisely in the presence of rhodium–copper alloys[56]. A more detailed description of the characteristic features of the reactions in the presence of alloys would be outside the framework of the present review; some additional information can be found in other reviews[166–170].

* * *

Significant progress has been achieved in recent years in the understanding of the mechanisms of catalytic reactions of hydrocarbons on metals. These advances are associated with the application of model compounds in catalysis, in particular those labelled with ^{13}C and ^{14}C, in combination with careful kinetic investigations. An important contribution to the understanding of the mechanisms of the above reactions in the presence of metal-containing catalysts undoubtedly came from a series of studies involving the participation of hydrogen in these reactions (see Section IV). A series of investigations of the influence of the structure of metallic catalysts on the mechanisms of different reactions is of fundamental importance (Section V).

However, in most cases the available information about the transition state in the key stages of the reactions of hydrocarbons is clearly inadequate and the structure of the catalytic centres and the relative positions of the orbitals of the surface metal atoms and the orbitals of the reacting atoms of the adsorbed molecules have not been elucidated. An important problem in the study of mechanism involves the investigation of the effect arising when the surface of the metal is acted upon by the reactants and products of the reaction in the course of its occurrence.

Studies carried out with the aid of a set of new physical methods whereby one can obtain information about the geometry of the adsorbed molecular fragments and the structure of the most active sections of the surface of the metal and the elucidation of the nature of the cluster and ligand effects in monometallic and polymetallic systems are at present the most important trends in the establishment of the mechanisms of the action of metal-containing catalysts.

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The Structure and Reactivity of Octadehydrocorrins and Corroles

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The review surveys the chemical properties of corroles, their metal complexes, and the metal complexes of octadehydrocorrins. The reactions of the metal complexes of octadehydrocorrins with electrophiles and nucleophiles, the interconversions of corrinoid compounds, the reactions involving the β,β-double bonds, and the acid-base properties and redox reactions of corrinoid compounds are considered. Problems of the structure of corroles, their metal complexes, and the metal complexes of octadehydrocorrins are discussed.
The bibliography includes 87 references.

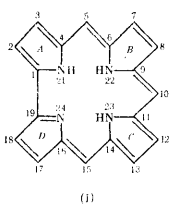
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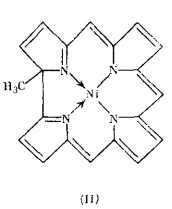
I. INTRODUCTION

Compounds containing the macrocyclic tetrapyrrole systems, which play an important role in biological processes, are presently arousing much interest. Such compounds include the metal complexes of porphyrins and corrins, which constitute the basis of many natural products involved in biocatalytic processes, for example haemin, chlorophyll, vitamin B_{12}, cytochrome *c*, and also the metal complexes of octadehydrocorrins.

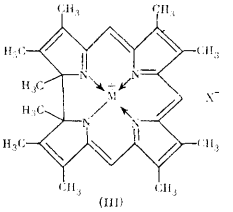
Corroles (I), the nickel complexes of 1-methyloctadehydrocorrins (II), and the metal complexes of 1,19-disubstituted octadehydrocorrins (III) have the steric structure of corrins and the degree of unsaturation of porphyrins, so that the study of their chemical and physicochemical properties makes a significant contribution to the development of the chemistry of tetrapyrrole macrocyclic compounds.



(I)



(II)



(III)

There are no reviews in the literature devoted directly to the chemical and physicochemical properties of octadehydrocorrins and corroles, but some problems have been considered in a review[1] and in a monograph[2] devoted to porphyrins. The present review deals with the available literature data on the chemical and physicochemical properties of corroles, their metal complexes, and the metal complexes of octadehydrocorrins.

II. THE STRUCTURE AND PHYSICAL PROPERTIES OF CORRINOIDS AND THEIR METAL COMPLEXES

1. Corroles

Corroles are crystalline red substances. They contain an aromatic 18π-electron cyclic system, indicated by the intense Soret band (~400 nm) in their absorption spectra, which contain in addition bands in the region of 540, 550, and 600 nm.[3] The mass spectrum of diethylhexamethylcorrole is very close to that of porphyrin and reflects the aromaticity and stability of corrole[4]. The aromatic properties of corroles are also indicated by their ^{1}H NMR spectra, in which the signals of the *meso*-protons are at 8.8–9.4 p.p.m. and those of the imino-protons are at ~–3.5 p.p.m.

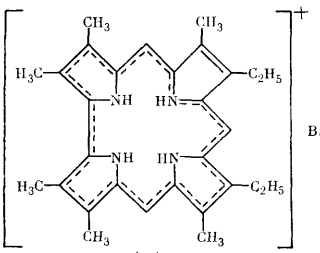
Quantum-chemical calculation of the distribution of π-electron density by the Pariser–Parr–Pople (PPP) method with the parameters of Nishimoto and Forster showed that the highest charge density is at the N atoms, while the π-electron density at the C atoms is enhanced in the 2-, 3-, and 10-positions[5].

The crystal and molecular structures of corrole[6], its hydrobromide (IV),[7] the copper complex of *N*-methylcorrole (Va),[8] the nickel complex of *N*-ethylcorrole (Vb),[9] the triphenylphosphinecobalt(III) complex of corrole (VI),[10] and the rhodium complexes of *N*-methylcorroles, (VII) and (VIII),[11] have not been determined.

8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole is not exactly planar[6]. Each of the four pyrrole rings is planar, the *A*, *B*, and *C* rings deviate from one another by only 1–3 degrees, while the *D* ring is inclined to the plane of the other rings at an angle of 8–10 degrees. The distances between the N atoms (2.89–2.53 Å) are shorter than in porphyrin (2.90 Å), but the length of three of these (2.89 to 2.66 Å) corresponds to the absence of strain. The N(21)–N(24) distance is 2.53 Å and the steric hindrance between these atoms affects the geometry of the *A* and *D* rings, in which the α,β-bonds are longer than the β,β-bonds. The three inner H atoms lie outside the plane of the macroring and are statistically distributed between the four N atoms[6].

However, quantum-chemical calculation by the PPP method of the bond length and the total π-electron energy of corrole for different dispositions of the inner H atoms shows that the fixation of these atoms in the 21-, 23-, and 24-positions is more probable[12]. The corrole model is asymmetric and has two forms [(+)- and (−)-] in the crystal, where the molecules are arranged in "parallel blocks"[6].

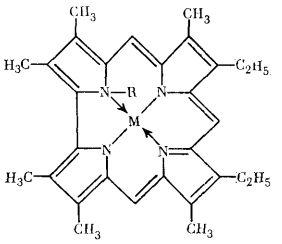
The bromine atom in corrole hydrobromide (IV) [7] is located above the centre of the corrole nucleus at the apex of a pyramid 2.58 Å high with a distorted square base made up of four N atoms. Three H atoms are involved in the formation of hydrogen bonds between the N and Br atoms.



(IV)

(a) R = CH_3, M = Cu

(b) R = C_2H_5, M = Ni



(V, a and b)

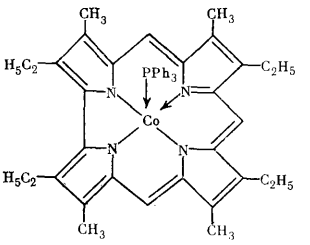
These bonds are non-linear and can bend. Two of them, involving the N(21) and N(23) atoms, are strong, the bond with the N(22) atom is weak, and the N(24)–H bond is directed towards the side away from the Br atom. The corrole system does not have a planar conformation.

The *B* and *D* rings are planar, while the *A* and *C* rings form a dihedral angle of 1–5 degrees along the line passing through the two α-carbon atoms. The N atoms of the *A* and *C* rings are inclined towards the Br atom, while the N atom of the *D* ring is inclined away from the Br atom. This is a result of two opposed effects—the opposite charges on the Br and N atoms and the overloading of the central part of the molecule by the N and H atoms. The *A* and *D* rings deviate in opposite directions, executing a twist around the C(1)–C(19) bond[7].

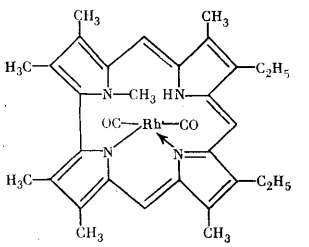
In the copper complex of N(21)-methylcorrole (Va) the *N*-alkylated *A* ring makes an angle of 23° relative to the molecular plane and the ring itself is bent along the line of the α-atoms by 10°, the β,β-bonds in this ring are longer than the α,β-bonds, and the N–CH_3 bond is longer than usual, its length amounting to 1.54 Å.[8]

In the nickel complex of N(21)-ethylcorrole (Vb) the *A* ring is also appreciably displaced from the molecular plane and the N atoms to which the C_2H_5 group is attached is to a large extent sp^3-hybridised[9].

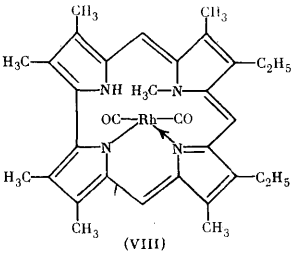
The triphenylphosphinecobalt(III) complex of corrole (VI) is formally a pentacoordinate square-pyramidal complex[10]. The corrole ligand is approximately planar, the N atoms projecting above the molecular plane by ~0.1 Å and the Co atom by 0.38 Å. The average Co–N distance (1.87 Å) is analogous to the corresponding distance in the cobalt complexes of corrins and is somewhat shorter than in porphyrins (1.98 Å). The molecules of complex (VI) have a distorted arrangement in the crystal[10].



(VI)



(VII)



(VIII)

An example of a non-planar complex is provided by the rhodium complexes of corrole (VII) and (VIII) [11] in which the N–CH_3 groups and the bis(dicarbonylrhodium) species are in the *trans*-positions. The pyrrole rings are approximately planar. The rings linked to rhodium are inclined towards it, while the other two rings are displaced in the oppsite direction. The average length of the Rh–N bond is 2.059 Å, being shorter than that of the similar bond in porphyrins (2.084 Å). The Rh...N distance in the *N*-methylated ring is greater by ~0.2 Å. The nitrogen atoms to which the CH_3 substituents are attached are sp^3-hybridised as in the *N*-alkylated copper[8] and nickel[9] complexes.

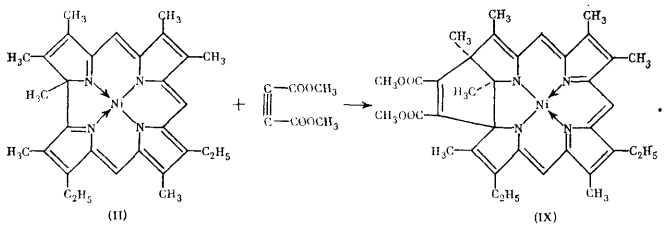
2. Metal Complexes of 1,19-Disubstituted Octadehydrocorrins

The metal complexes of 1,19-disubstituted octadehydrocorrins are high-melting crystalline substances with a violet or dark cherry-red colour. These are salts with a tetragonal-pyramidal structure where the tetradentate heterocyclic octadehydrocorrin system is the equatorial ligand, while the axial ligand (the anion) is at the apex of the pyramid. The cobalt(II) complexes of octadehydrocorrins are low-spin complexes with an unpaired electron in the d_{z^2} orbital of the cobalt atom oriented at right angles to the plane of the macroring[13,14]. The electronic spectra of the metal complexes of octadehydrocorrins contain three main absorption bands in the regions 280–300, 350–365, and 500–580 nm, but do not have a Soret band. The ^{1}H NMR spectra lead to the conclusion that the metal complexes of octadehydrocorrins occupy an intermediate position between those of the aromatic metal complexes of porphyrins and the non-aromatic corrin complexes. The signals of the *meso*-protons of the nickel complexes of octa-alkyl-1,19-dimethyloctadehydrocorrins are at ~7.5 p.p.m.[15], while the signals of the *meso*-protons of the nickel complexes of porphyrins are at ~11 p.p.m.[16] and those of the nickel complexes of corrins are at 5.9–6.4 p.p.m.[17]

3. Nickel Complexes of 1-Alkyloctadehydrocorrins

1-Alkyloctadehydrocorrins are neutral metal complexes. Only the nickel(II) complexes are known. The signals of the *meso*-protons of these complexes are at 6.0–7.0 p.p.m.[18]

1-Alkyloctadehydrocorrins exhibit the properties of unsaturated compounds; they enter into the Diels–Alder reaction with dimethylacetylenedicarboxylate to form the adduct (IX):[2]



(II) (IX)

III. THE ACID–BASE PROPERTIES OF CORRINOIDS AND THEIR METAL COMPLEXES

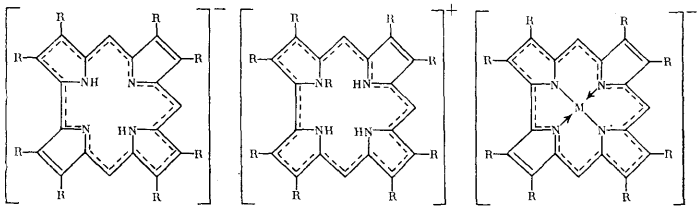
Tetrapyrrole macrocyclic compounds of all kinds react with both acids and bases.

1. The Acid–Base Properties of Corroles and Their Metal Complexes

On treatment with dilute alkali, corroles are converted into the stable aromatic anions (X).[3,19,20] The enhanced acidity of corrole may be explained by the steric hindrance between the imino-hydrogen atoms.

Corroles readily undergo monoprotonation[3,19,20] on treatment with dilute HBr in acetone; the crystalline monobromides formed are aromatic ambident cations (IV) whose charge is delocalised over the macroring[19]. On treatment with concentrated H_2SO_4, CF_3COOH,[3] or FSO_3H,[19,21] corrole is converted into a non-aromatic dication, from which the non-protonated corrole is reformed on treatment with alkali[19]. The ability of corrole to both give up a proton and to combine with one indicates the delocalisation of the free electron pair over all four nitrogen atoms.

N-Alkylcorroles are more basic than the initial corrole. Protonation of the N(21)- and N(22)-methylcorroles takes place when they are merely dissolved in acetic acid with formation of the aromatic monocations (XI).[22] In a 1 M solution of H_2SO_4 in acetic acid, *N*-methylcorroles are converted into dications whose spectra contain the Soret band, which rules out the breakdown of conjugation in the chromophore, but the site of addition of the second proton could not be established.

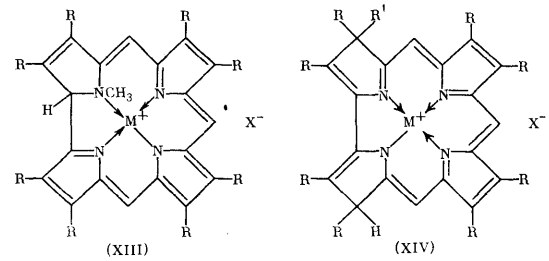


(X) (XI) (XII, a and b), (a) M = Ni; (b) M = Cu

With increasing H_2SO_4 concentration, a third proton adds to the *N*-methylcorrole, apparently at the C(5) atom[22]. The same substance is formed on dissolution of *N*-alkylcorroles in CF_3COOH.[19]

The nickel and copper complexes of corroles are relatively stable[3]. On treatment with alkalies, they are converted into the stable aromatic ambident anions (XII, a and b), whose electronic spectra contain the Soret band[20,23–25].

The nickel complexes of *N*-methylcorroles are protonated in the angular position on dissolution of CF_3COOH with formation of the non-aromatic compound (XIII) whose electronic spectrum is similar to that of the nickel complex of 1-methyloctadehydrocorrin[9,26]. The protonation of the palladium complexes of N(21)-alkylcorroles takes place analogously[27].



(XIII) (XIV)

M = Ni, Pd

Angular protonation of the nickel and palladium complexes of 3,3-dialkylcorroles, which causes the breakdown of the conjugation chain, is less favourable than the *N*-protonation[26–29] and on dissolution of the nickel complexes of 3,3-dialkylcorroles in CF_3COOH, the proton adds to the 17-position with formation of the complex (XIV).[26,29] The protonation of the palladium complexes of 3,3-dialkylcorroles takes place analogously[27,28].

The pyridinium salt of the palladium complex of corrole is diprotonated in CF_3COOH in the 3- and 17-positions, which results in the formation of the complex (XIV), where R′ = H.[27]

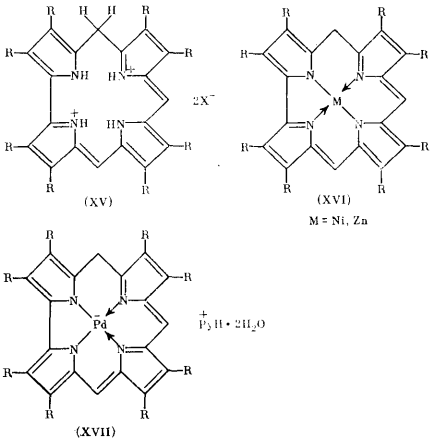
Treatment of a solution of the square-planar cobalt(III) complex of corrole or any other pentacoordinate derivative with HBr in acetone leads to the formation of a green crystalline paramagnetic hydrobromide in which the protonation site has not been established[30]. When $HClO_4$ is added to a solution of Co-corrole in tetrahydrofuran (THF), the monoprotonated Co-corrole is formed, whose electronic spectrum resembles that of Ni-corrole[13]. The protonation of Co-corrole is reversible and the addition of pyridine results in the formation of the non-protonated pyridinecobalt(III) complex of corrole[30].

2. The Interaction of Corroles with Metals

The free bases of corroles readily react with metal cations to form metal complexes. Corrole is a tetradentate ligand, where three out of the four N atoms are linked to hydrogen atoms capable of being substituted. In the formation of metal complexes of corroles, all three, two, or one hydrogen atoms are substituted by the metal depending on the nature of the latter.

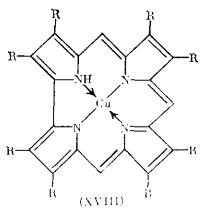
When corrole is treated with solutions of nickel, copper, zinc, and palladium salts[3,27] in the presence of bases, only two hydrogen atoms are substituted by the metal and the products are metal complexes of corroles derived from the non-aromatic base corresponding to the dication (XV),[3,9,26,27] the third hydrogen atom passing to one of the carbon atoms of the macroring and disrupting the aromatic conjugation system of corrole[21]. Its location at C(10) [27,31] or C(5) [21]

has not been finally established. Structure (XVI) is more probable. The palladium complex has been isolated as the dihydrate of the pyridinium salt (XVII), which is formed when corrole is treated with $(CH_3COO)_2Pd$ in pyridine[27].



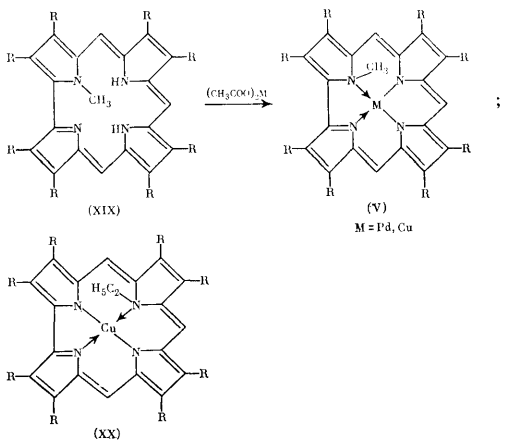
(XV) (XVI) M = Ni, Zn (XVII)

The visible spectra of the copper complexes differ from those of the nickel and palladium complexes and are analogous to the spectra of the copper complexes of N(21)-methylcorroles, indicating at the same time the retention of the conjugated system of the macroring. Structure (XVIII), where the "extra" hydrogen is located at the N(21) atom, was therefore proposed for the copper complexes of corroles[21].



(XVIII)

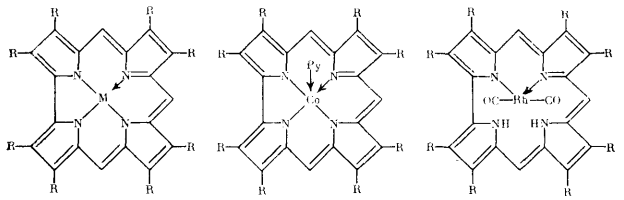
N-Alkylcorroles readily react with metal salts. Treatment of N(21)-methylcorrole (XIX) with $(CH_3COO)_2Pd$ or $(CH_3COO)_2Cu$ yielded the palladium and copper complexes of N(21)-methylcorrole [compounds (V)].[21,27,28] The copper complex of N(22)-ethylcorrole (XX) was obtained analogously by the reaction of $(CH_3COO)_2Cu$ with N(22)-ethylcorrole[21,27,28]:



(XIX) (V) M = Pd, Cu (XX)

The reaction of zinc salts with *N*-alkylcorroles leads to the formation of unstable products[28], while nickel salts do not react with *N*-alkylcorroles[9,28]. The interaction of N(21)-alkylcorroles (XIX) with the perchlorate of the hexamethylnickel cyanide complex leads to the formation of the corresponding nickel complex (V, M = Ni).[9] The metal complexes of *N*-alkylcorroles are aromatic: the signals of their *meso*-protons in the ^1H NMR spectra are at 9.0–9.3 p.p.m.[9,27]

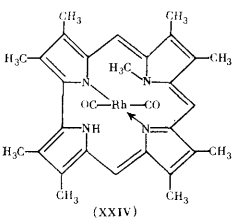
When an attempt is made to insert bivalent cobalt into N(21)-methylcorrole (XIX), the methyl group is split off and all three imino-protons are substituted by the metal with formation of the cobalt(III) complex of the *N*-unsubstituted corrole (XXI).[21,30] The complexes (XXI) are square-planar paramagnetic compounds. When corrole is treated with $(CH_3COO)_2Co$ in the presence of pyridine, purple prismatic crystals of the pentacoordinate pyridinecobalt(III) complex of corrole (VIa) are formed[30]; the latter readily splits off pyridine on treatment with hot methanol[3] and is converted into the planar tetracoordinate complex (XXI).[30] The pentacoordinate complexes (VI) are also formed in the presence of $(C_6H_5)_3P$ and p-$CH_3C_6H_4NC$.[30]



(XXI), (XXII), M = Co, Fe (VIa) (XXIII)

A crystalline paramagnetic iron(III) complex of corrole (XXII) has been synthesised by treating the corrole anion (X) with $FeCl_3$.[30]

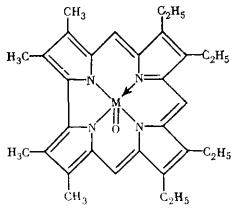
Rhodium complexes of corroles have been obtained quite recently[11,32,33]. The interaction of corrole with $RH_2(CO)_4Cl_2$ leads to the formation of the monorhodium complex of corrole (XXIII). The reaction of N(21)-methylcorrole (XIX) with $Rh_2(CO)_4 \cdot Cl_2$ in chloroform containing CH_3COONa leads to the formation of the complex (VII).[11]



(XXIV)

On interaction with an excess of $Rh_2(CO)_4Cl_2$ at room temperature, N(22)-methylcorrole gives rise to a mixture of the complex (VIII) and (XXIV), the complex (VIII) being converted into the complex (XXIV) on standing. The molybdenum and chromium complexes of corrole have been synthesised after the discovery of superconducting materials[34] in an attempt to obtain an electrical conductor in the form of metal complex species with a metal–metal bond stacked one on top of the other. When corrole was allowed to interact with $MoCl_5$ or $Mo(CO)_6$ at 170–180 °C in nitrogen, the complex (XXV) was obtained. It is a monomeric pentacoordinate oxomolybdenum complex with an axial disposition of the oxygen atom[35]. Its symmetry is close to that of a tetragonal pyramid. In the electronic spectrum there is a Soret band. The EPR spectra indicate a π-bonding interaction between the Mo and O atoms.

There is a considerable contribution of the π-interaction in the plane of the macroring between the Mo atom and the electron-donating N atom; the coordinate bonds have a high degree of covalence[34].

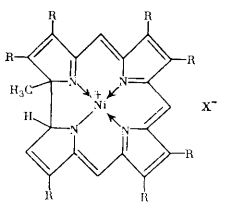


(XXV), (XXVI), M = Mo, Cr

The oxochromium complex (XXVI) has been synthesised by treating corrole with $CrCl_2$ in dimethylformamide (DMF) in the presence of sodium acetate[36]. This is an N_4O-pentacoordinate complex with a symmetry close to that of a tetragonal pyramid[37]. The unpaired electron is in the $3d_{xy}$ orbital of chromium and there is a strong interaction between this orbital and the σ and/or π orbitals of the macroring[36].

3. Protonation of the Metal Complexes of Octadehydrocorrins

The nickel(II) complexes of 1-methyloctadehydrocorrins are effective electron donors and, on treatment with strong acids ($HClO_4$, CF_3COOH, FSO_3H), they are protonated in the 19-position with formation of salts of the nickel complexes of 1-methyloctadehydrocorrins (XXVII);[18,21,38–41] the corresponding perchlorate has been isolated in a crystalline form[39]. The protonation of 1-methyloctadehydrocorrins is reversible and treatment of the salts (XXVII) with alkali results in the reformation of the initial complexes of 1-methyloctadehydrocorrins.



(XXVII)

The metal complexes of 1,19-dimethyloctadehydrocorrins are capable of being protonated in a strongly acid medium[42]. When nickel and cobalt complexes of octadehydrocorrins are dissolved in concentrated sulphuric acid, a proton apparently adds to N(21) or N(24) with formation of an intramolecular hydrogen bond. In addition, the protonated form is probably a radical-cation, which is indicated by the intense absorption at 690 nm, characteristic of the free radicals of cyanonickel complexes of octadehydrocorrins[43]. The protonation of metal complexes of octadehydrocorrins is reversible and dilution of their sulphuric acid solutions with water leads to the reformation of the initial complexes[42].

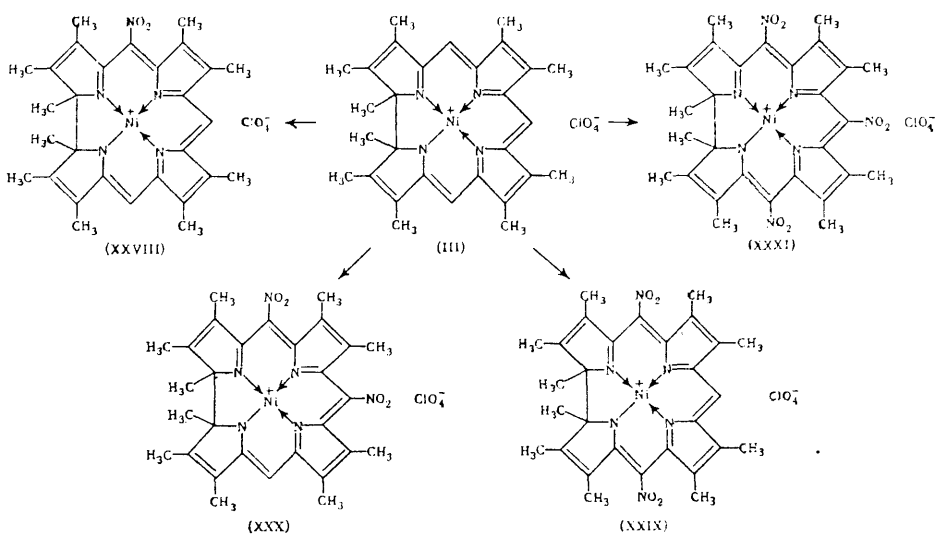
4. Deuterium Exchange

Corrinoid systems of all types are capable of deuterium exchange. Corroles exchange rapidly all three *meso*-hydrogen atoms for deuterium in CD_3COOD.[3] The exchange of all the *meso*-hydrogen atoms of 3,17-diethoxycarbonyl-8,12-diethyl-2,7,13,18-tetramethylcorrole in a mixture of CF_3COOD and $CDCl_3$ at room temperature takes place over a period shorter than 10 min.[19,44,45] The half-exchange period for the proton in the 10-position in the nickel complex of octa-alkyl-1-methyloctadehydrocorrins in CF_3COOD at 35 °C is 15 min, while that for the proton in the 5-position is 11–15 min.[40] In the presence of free β-positions in the octadehydrocorrin macroring, the β-proton exchanges for deuterium[29]. The nickel complex of hexa-alkyl-1,19-dimethyloctadehydrocorrin in CF_3COOD apparently exchanges the *meso*-hydrogen atoms as well as the β-hydrogen atoms.

IV. REACTIONS WITH ELECTROPHILES AND NUCLEOPHILES

1. Electrophilic Substitution Reactions

In the metal complexes of octadehydrocorrins the equatorial ligand is the tetrapyrrole macroring containing an extensive system of conjugated C=C and C=N bonds. The presence of this system is responsible for the ability of these compounds to react with electrophiles.

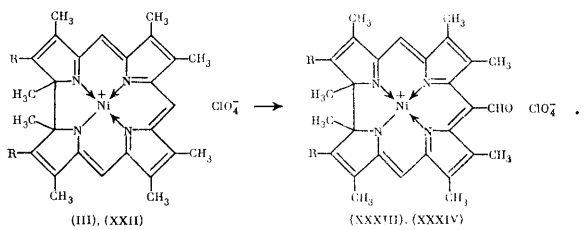


(XXVIII) (III) (XXXI)

(XXX) (XXIX)

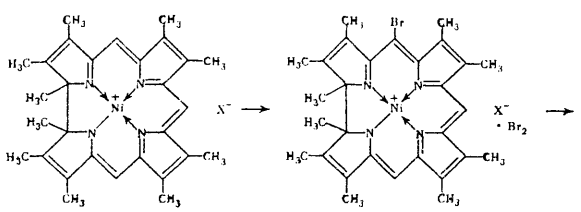
The nickel complexes of octadehydrocorrins are readily nitrated. Treatment of the nickel complex of decamethyl-octadehydrocorrin (III) with fuming HNO_3 and urea at 0 °C yielded the perchlorate of the nickel complex of 5-nitro-octadehydrocorrin (XXVIII).[46] The 5-nitro-derivative is also formed on treatment of the nitrate of the nickel complex of 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyloctadehydro-corrin with $Cu(NO_3)_2$ in acetic anhydride[43,47]. Treatment of the complex (III) with the 1 : 1 mixture of fuming HNO_3 and concentrated H_2SO_4 at 0 °C leads to the formation of a mixture of the perchlorates of the nickel complexes of the 5,10-dinitro derivative (XXIX) and the 5,15-dinitro derivative (XXX). Under more severe conditions, in the 1 : 1 mixture of HNO_3 and oleum, the nickel complex of 5,10,15-trinitro-octadehydrocorrin (XXXI) was isolated[46].

The nickel complexes of octadehydrocorrins readily undergo the Vilsmeier reaction, which takes place more readily with aromatic compounds having an enhanced activity with respect to electrophilic substitution. When the perchlorates of the nickel complexes of decamethyloctadehydrocorrin and octa-methyloctadehydrocorrin (XXXII) in boiling $CHCl_3$ are treated with $POCl_3$ and DMF, the nickel complexes of the corresponding 10-formyloctadehydrocorrins (XXXIII) and (XXXIV) are formed[48], their formyl groups readily forming bisulphite derivatives.



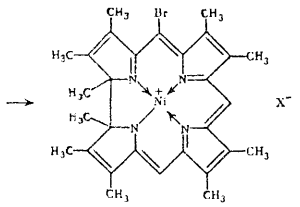
(III), (XXII) (XXXIII), (XXXIV)

Depending on the reaction conditions, the halogenation of the salts of the nickel complexes of octadehydrocorrins leads to the formation of mono- or di-halogeno-derivatives. When the perchlorate and nitrate of the nickel complex of deca-methyloctadehydrocorrin (III, a and b) are treated with bromine in acetic acid, the perchlorate and bromide of the nickel complexes of 5-bromo-octadehydrocorrin (XXXV, a and b) are formed[49], i.e. the substitution reaction is accompanied by the replacement of the NO_3^- anion by the Br^- anion. The two compounds (XXXV, a and b) contain two additional Br atoms, which are not substituents in the macro-ring and are readily removed on treatment with acids or bases with formation of the complexes (XXXVI, a and b):



(III, a and b)
X = ClO_4, NO_3

(XXXV, a and b)
X = ClO_4, Br



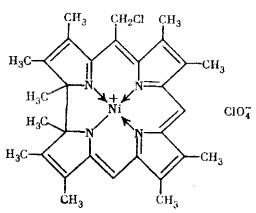
(XXXVI, a and b)

The bromination of the nickel complexes of octadehydro-corrins with bromine in $CHCl_3$ [49] or $C_2H_4Cl_2$ [43] yielded the nickel complexes of 5,10-dibromo-octadehydrocorrins; when hydroquinone was added, 5-bromo-octadehydrocorrin was isolated. The chlorination of the nickel complex of deca-alkyloctadehydrocorrin with chlorosuccinimide leads to the formation of the *meso*-dichloro-derivative[43]. Bromination with Br_2 in acetic acid is an electrophilic substitution reaction, while bromination with Br_2 in $CHCl_3$ and $C_2H_4Cl_2$ and chlorination with chlorosuccinimide takes place via a radical mechanism, i.e. electrophilic halogenation leads to the formation of 5-halogeno-derivatives, while radical halogenation results in the formation of 5,10-dihalogeno-derivatives.

The halogens in the *meso*-positions in octadehydrocorrins are readily substituted by hydrogen in the presence of traces of acid[43]. The debromination of the nickel complex of 5-bromo-octadehydrocorrin (XXXV) takes place when it is dissolved in nitromethane, apparently via the following reaction[49]:

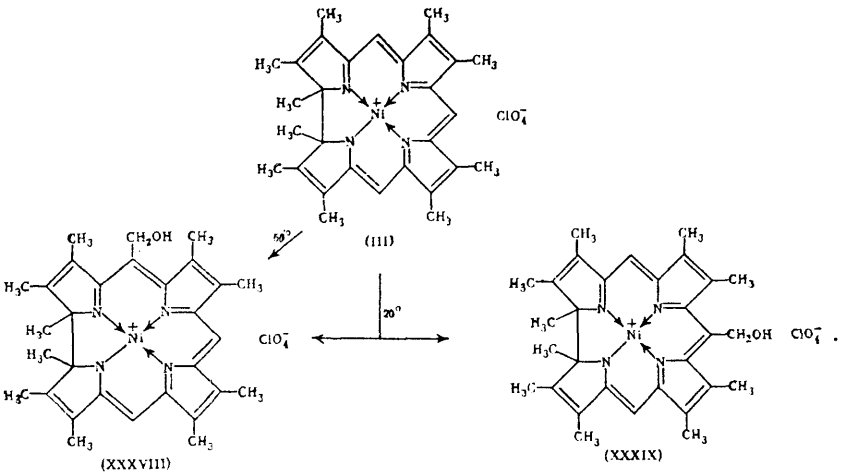
$$\text{C}{-}\text{Br} + CH_3NO_2 \rightarrow \text{C}{-}\text{H} + CH_2BrNO_2 \ .$$

The nickel complexes of octadehydrocorrins readily undergo the chloromethylation reaction, which consists in the direct substitution of hydrogen by the CH_2Cl group on treatment with paraformaldehyde and concentrated HCl in glacial acetic acid. The chloromethylation of the nickel complex of decamethyloctadehydrocorrin led to the isolation of the nickel complex of 5-chloromethyloctadehydrocorrin (XXXVII), i.e. the product of the introduction of one CH_2Cl group into the octadehydrocorrin macroring[50].

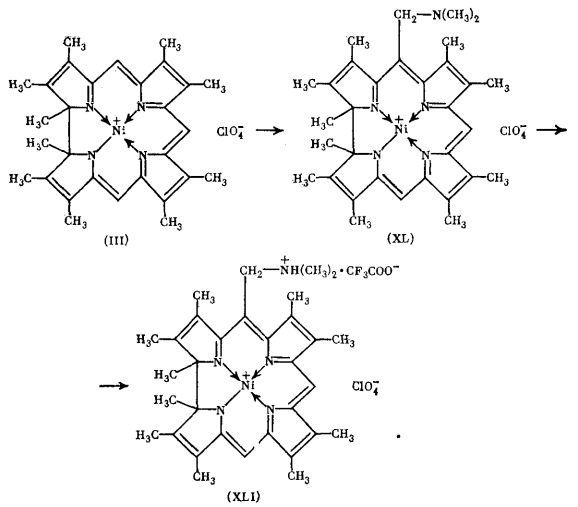


(XXXVII)

Treatment of the nickel complex of decamethyloctadehydro-corrin with paraformaldehyde in glacial acetic acid leads to the formation of the mono-*meso*-hydroxymethyl derivatives (XXXVIII) and (XXXIX).[50] The mode of reaction depends on temperature: the 5-hydroxymethyl derivative (XXXVIII) is formed at 50 °C, while at room temperature there are two products: 5-hydroxymethyloctadehydrocorrin (XXXVIII) and 10-hydroxymethyloctadehydrocorrin (XXXIX):



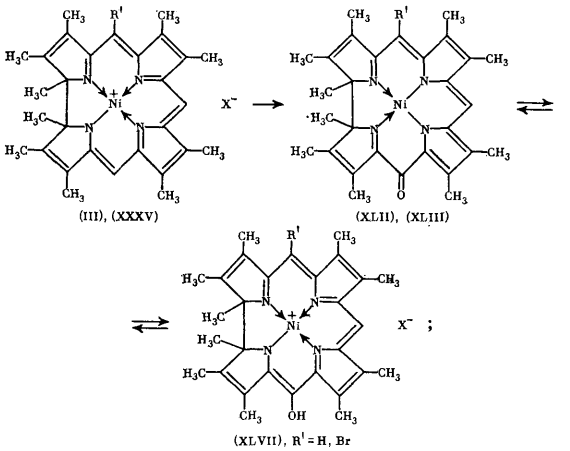
The reaction of the perchlorate of the nickel complex of decamethyloctadehydrocorrin with formaldehyde and dimethylamine in alcohol yielded the nickel complex of 5-dimethylaminomethyloctadehydrocorrin (XL), which is protonated in CF_3COOH and converted into the perchlorate of the nickel complex of decamethyloctadehydrocorrin (XLI) containing the $CH_2^+NH(CH_3)_2.CF_3COO^-$ substituent:[51]



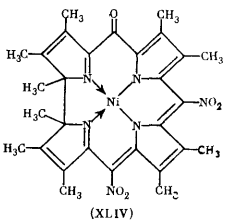
2. Reactions with Nucleophiles

The positive charge in salts of the metal complexes of octadehydrocorrins is not fixed at the central metal atom but is delocalised over the octadehydrocorrin macroring[21]. The delocalisation has a major influence on the chemical behaviour of octadehydrocorrins. In particular, the cationic forms of the nickel complexes of octadehydrocorrins are very sensitive to attack by nucleophiles.

The salts of the nickel complexes of octadehydrocorrins are converted into neutral oxo-complexes on treatment with bases in air[21,43,49,52]. When the nickel complex of decaalkyloctadehydrocorrin, for example, compound (III), was treated with an aqueous solution of NaOH, an excess of $(C_2H_5)_3N$, or CH_3Li in moist THF,[43] the nickel complex of 5-oxo-octadehydrocorrin (XLII) was obtained.

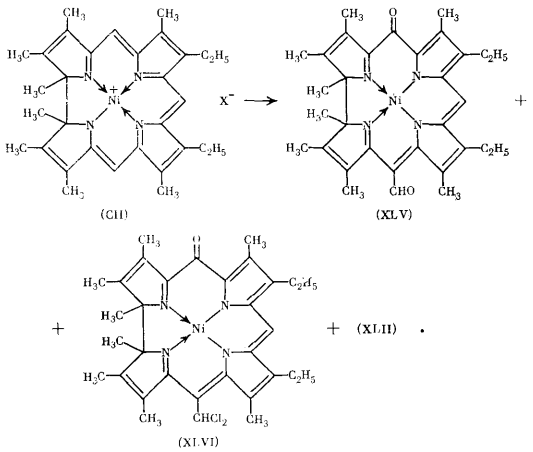


The reaction of the nickel complex of 5-bromo-octadehydrocorrin (XXXV) with a 5% NaOH solution in 30% H_2O_2 leads to the nickel complex of 5-bromo-15-oxo-octadehydrocorrin (XLIII).[49]



Nitration of the nickel complex of decamethyloctadehydrocorrin with a mixture of fuming HNO_3 and glacial acetic acid at 0 °C yielded the nickel complex of 10,15-dinitro-5-oxo-octadehydrocorrin (XLIV),[49] while the addition of an aqueous NaOH solution to a chloroform solution of the nickel complex (CII) at room temperature led to the isolation, together with the nickel complex of 5-oxo-octadehydrocorrin (XLII), of the complexes of 15-formyl-5-oxo-octadehydrocorrin (XLV) and

15-dichloromethyl-5-oxo-octadehydrocorrin (XLVI):[43]

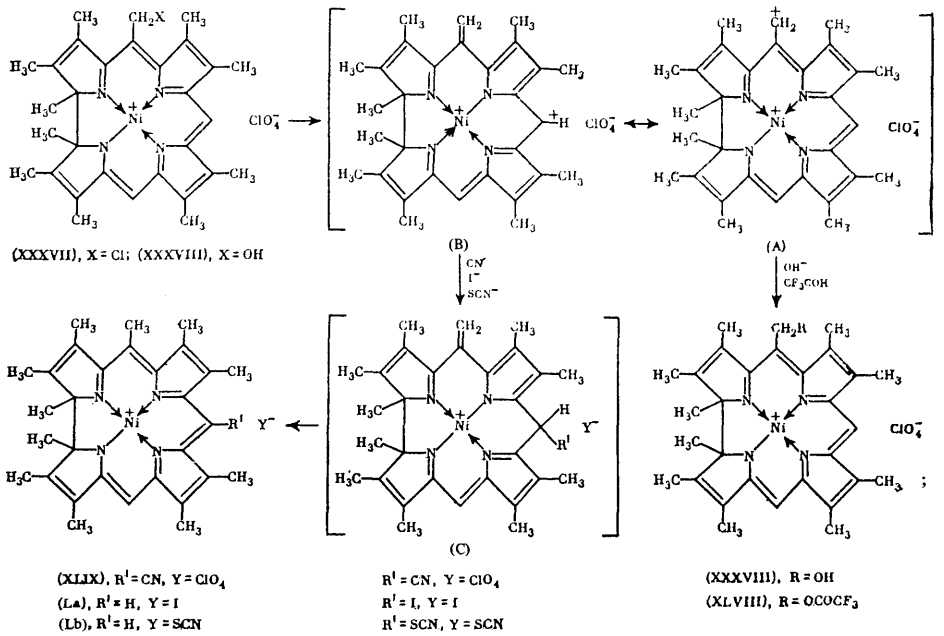


The conversion of the salts of the nickel complexes of octadehydrocorrins into neutral 5-oxo-derivatives probably proceeds as follows: initially the nucleophile adds on and the carbanion is formed, the latter being oxidised by atmospheric oxygen to the neutral nickel complex of oxo-octadehydrocorrin. The presence of electron-accepting substituents in octadehydrocorrin macrorings facilitates this reaction. In contrast to the nickel complexes, the cobalt complexes of octadehydrocorrins with electron-accepting substituents in the macroring are readily converted into cobalt(I) derivatives on treatment with bases. A whole series of oxo-complexes of substituted octadehydrocorrins, containing the $CHCl_2$, Br, CN, CHO, NO_2, and NH_2 groups in the *meso*-positions, have been obtained. The nitro-groups in the oxo-complexes are readily split off in an acid medium[43].

The oxo-group in the nickel complexes of octadehydrocorrins does not exhibit certain properties characteristic of this group. Thus, it has not been possible to convert the nickel complexes of oxo-octadehydrocorrins into the enolic forms[40]. However, when these compounds are dissolved in CF_3COOH, they are *O*-protonated with formation of hydroxy-forms, which could not be isolated. The hydroxy-complex (XLVII) is converted into the oxo-form on treatment with alkali[43,49].

The nickel complexes of octadehydrocorrins with the CH_2OH and CH_2Cl groups in the 5-position exhibit a dual reactivity in reactions with nucleophiles[51,53]. When the nickel complex of 5-chloromethyloctadehydrocorrin (XXXVII) was refluxed with a NaOH solution in alcohol, the nickel complex of 5-hydroxymethyloctadehydrocorrin (XXXVIII) was isolated and treatment with CF_3COOH resulted in the nickel complex of 5-trifluoroacetoxymethyloctadehydrocorrin (XLVIII). The reactions of the nickel complexes of 5-chloromethyloctadehydrocorrin and 5-hydroxymethyloctadehydrocorrin (XXXVIII) with KCN, KI, and KSCN proceed differently. When the nickel complexes of 5-hydroxymethyl- (XXXVIII) and 5-chloromethyl-octadehydrocorrins were treated with a solution of KCN in aqueous alcohol at room temperature, the nickel complex of 10-cyano-1,2,3,5,7,8,12,13,17,18,19-undecamethyloctadehydrocorrin (XLIX) was isolated in both cases, i.e. the reaction with the CN^- anion proceeds with transfer of the reaction centre. When the complexes (XXXVII) and (XXXVIII) were treated with KI or KSCN, the nickel complex of undecamethyloctadehydrocorrin (L, a and b) was isolated as the iodide or thiocyanate respectively[53]:

The following reaction mechanism has been proposed: the heterolysis of the C–X bond results in the formation of an ambident cation, whose stability is enhanced owing to the redistribution of electron density as a result of the delocalisation of the positive charge over the π-electron system of the macroring. The resonance structures of the carbonium ion (A) and (B) are possible. The addition of the nucleophile to the CH_2^+ group results in the formation of the CH_2X derivative and attack on the *meso*-carbon atom produces the intermediate compound (C), which is converted into a 10-substituted 5-methyloctadehydrocorrin after the migration of the proton from the *meso*-position to the methylene group. The *meso*-iodo- and *meso*-thiocyanato-derivatives readily lose

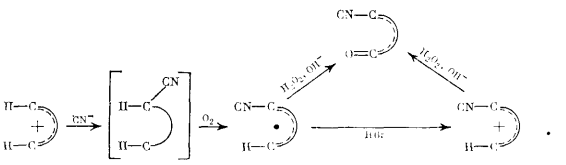


these substituents, being converted into undecamethyloctadehydrocorrin (L, a and b). The nature of the nucleophile determines the mode of reaction. This behaviour has been interpreted[51,53] on the basis of the principle of the hard and soft acids and bases (HSAB).[54,55] The CH_2^+ reaction centre formally corresponds to a hard acid, since there is a smaller possibility of the delocalisation of the charge on the primary carbon atom and, according to the HSAB principle, it should be coordinated preferentially to hard bases, i.e. OH^- and CF_3COO^-, while the reaction centre at the *meso*-carbon atom can be regarded as a soft acid which reacts preferentially with CN^-, I^-, and SCN^-.

The cationic forms of the nickel complexes of octadehydrocorrins exchange anions in the course of the reactions of the perchlorates of the nickel complexes (XXXVII) and (XXXVIII) with KSCN and KI. When the complexes (L, a and b) are dissolved in CF_3COOH, I^- and SCN^- are replaced by the CF_3COO^- anion.

The oxidation of the nickel complexes of octadehydrocorrins to the oxo-complexes on treatment with nucleophiles is sometimes accompanied by a nucleophilic substitution reaction. Several instances of nucleophilic substitution without the oxidation of the macroring are also known. When the nickel complexes of 5,10-dibromo- and 5,10-dichloro-octadehydrocorrins are treated with CH_3Li in moist THF, the formation of the oxo-complexes is accompanied simultaneously by the nuclophilic exchange of the halogens for hydrogen, while on treatment with $LiCu(CH_3)_2$ the complexes are converted into 5,10-dimethyloctadehydrocorrins[38].

The interaction of the nickel complexes of *meso*-unsubstituted octadehydrocorrins with KCN in CH_3OH leads rapidly to the formation of three products: the neutral 15-cyano-5-oxo-octadehydrocorrin and the free radicals of 5-cyano- and 5,15-dicyano-octadehydrocorrins[56,57], whose unpaired electron is delocalised over the macroring. Treatment of the radical of 5-cyano-octadehydrocorrin with HBr yielded the bromide of the nickel complex of 5-cyano-octadehydrocorrin. The oxidation of this complex with an alkaline solution of hydrogen peroxide led to the formation of the nickel complex of 5-cyano-15-oxo-octadehydrocorrin:



Treatment of the radical of dicyano-octadehydrocorrin with $HClO_4$ converts it into the perchlorate of the nickel complex of dicyano-octadehydrocorrin. This salt can be readily converted into a radical when it is chromatographed on Al_2O_3. The introduction of the cyano-group and oxidation of the salt of the nickel complex of 5-cyano-octadehydrocorrin leads to the formation of a dicyano-octadehydrocorrin radical and then a salt of the nickel complex of 5,15-dicyano-octadehydrocorrin[56,67].

V. ALKYLATION OF CORRINOIDS AND THEIR METAL COMPLEXES

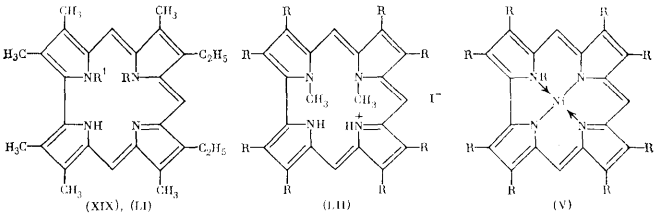
1. Alkylation of Corroles and Their Metal Complexes

Corrinoid macrocyclic compounds of all types undergo the alkylation reaction, but for each type of compound the reaction proceeds differently.

The alkylation of corroles and their metal complexes takes place at the nitrogen atoms. The reaction of the corrole anion, formed in the presence of K_2CO_3, with alkyl halides leads to the formation of a mixture of N(21)-alkylcorroles (XIX) and N(22)-alkylcorroles (LI), where R or R′ = CH_3, C_2H_5, $CH_2CH{=}CH_2$, or $(CH_3)_2C{=}CH_2$.[3,9,19,28] The N(21)-isomers are formed preferentially. In the absence of bases, alkylation does not occur. In the methylation of corrole having the $COOC_2H_5$ substituents in the 3- and 17-positions, the deactivating influence of these groups leads to the preferential formation of N(22)-methylcorrole[45].

(N(21)-Alkylcorroles are more stable than N(22)-alkylcorroles. Both isomers are aromatic and their electronic spectra contain the Soret band[28]. *N*-Alkylation increases the basicity of corroles, N(21)-methylcorroles being less basic than the N(22)-isomers: the relative acid dissociation constants of the monocations of N(21)- and N(22)-methylcorroles are 0.35 and 1.28 respectively[22].

The methylation of *N*-methylcorroles under severe conditions, for example treatment of N(21)- and N(22)-methylcorroles with CH_3I in sealed tubes (for 15 h at 100 °C) leads to the formation of N(21), N(22)-dimethylcorrole (LII), which was isolated as the iodide.

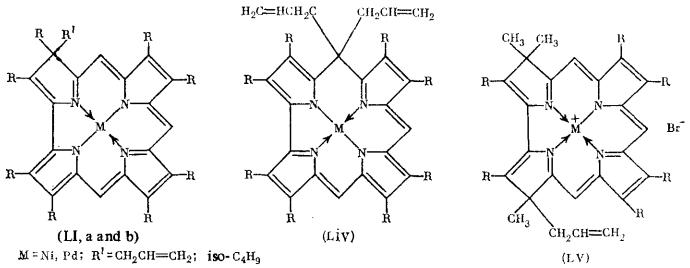


The *trans*-disposition of the *N*-alkyl groups in *N*,*N*-dialkylcorroles was demonstrated in a study of the optical rotation of a D-camphor-10-sulphonate salt[28]. The free base could not be obtained from the salt (LII). Under the same conditions, the *N*-unsubstituted corrole is also converted into *N*,*N*-dimethylcorrole and the *N*-monomethylcorrole was not isolated. Thus the rate of introduction of the second CH_3 group is higher than that of the first, i.e. *N*-alkylcorroles are more nucleophilic and basic than the *N*-unsubstituted corrole. The N(21), N(22)-dimethylcorrole salt (LII) is thermally unstable and on heating in boiling $C_6H_4Cl_2$ is converted into N(21)-methylcorrole[19]. The increased basicity of *N*,*N*-dialkyl-substituted macrocyclic compounds is a common property of corroles and porphyrins[58].

The acetylation of corroles takes place analogously to their alkylation[19]. When corrole is refluxed with acetic anhydride, N(21)-acetylcorrole is formed, its electronic spectra differing from the spectra of N(21)-alkylcorrole by the bathochromic shift of the absorption bands. The infrared spectrum of *N*-acetylcorrole has an absorption band at 1709 cm^{-1}, whose position indicates the absence of conjugation of the CO group with the chromophore of the macrocyclic compound. On an Al_2O_3 column or on treatment with NaOH, *N*-acetylcorrole is converted into *N*-unsubstituted corrole[19].

The nickel complexes of corrole anions also readily react with alkyl halides, which results in the formation of aromatic and diamagnetic N(21)-alkyl derivatives (V) whose additional alkyl group is shielded (τ = 12.6) and the molecule has no symmetry plane[9,23,26]. The reaction of the nickel complex of the corrole anion with $CH_2{=}CHCH_2Br$ leads to the formation of a mixture of the complexes of 3-alkyl-3-allylcorrole (LIII) and 5,5-diallylcorrole (LIV).[9,23,26] The nickel complex of 3-allyl-3-methylcorrole is apparently formed from the *N*-allyl

derivative via a [1,5]- or [3,3]-sigmatropic rearrangement. After the alkylation of the nickel complex with $(CH_3)_2C=CHCH_2Br$, triallylcorrole and *meso*-diallylcorrole (LIV) were isolated in addition to the 3-allyl derivative. The *meso*-derivative is not a product of the rearrangement of 3-allylcorrole, since the latter does not rearrange. The reaction of the nickel complex of corrole with isobutyl iodide leads to the formation of the 3-isobutyl derivative (LIIIb). This mode of reaction with $CH_2=CHCH_2Br$ and iso-C_4H_9I is probably due to steric factors[9].



(LI, a and b) (LIV) (LV)

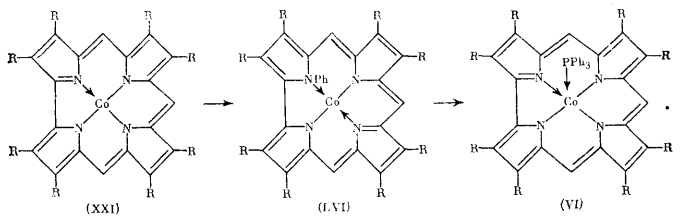
M = Ni, Pd; $R^1 = CH_2CH=CH_2$; iso-C_4H_9

The alkylation of the nickel complex of 3,3-dialkylcorrole (LIII) with $CH_2=CHCH_2Br$ or $C_6H_5CH_2Cl$ takes place in the 17-position with formation of the salt (LV).[9]

The methylation of the pyridinium salt of the palladium complex of corrole (XVII) with CH_3I in boiling acetone in the presence of NaOH results in the formation of N(21)-methylcorrole (V, M = Pd) and 3,3-dimethylcorrole (LIII). The alkylation of the palladium complex of 3,3-dialkylcorrole with $CH_2=CHCH_2Br$ yields the palladium complex of 3,3,17-trialkyl-17-allylcorrole (LV).[27]

The alkylation of the copper complexes of corroles leads to the formation of the N(21)-alkyl derivatives[9,27,28], which split off the *N*-alkyl group on heating in 1-chloronaphthalene[27].

Treatment of a solution of the cobalt(III) complex of corrole (XXI) in THF with C_6H_5MgBr or C_6H_5Li results in the formation of the green crystalline cobalt(II) complex of N(21)-phenylcorrole (LVI).[30] The *N*-*p*-tolyl derivative was obtained in the same way.

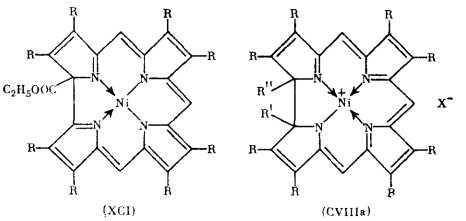


(XXI) (LVI) (VI)

Arylated Co-corroles are paramagnetic and non-planar. They are stable in the light both in the solid state and in solutions and do not form pentacoordinate cobalt(III) complexes of corroles on heating with pyridine or triphenylphosphine. The aryl group is split off at 130 °C and the resulting Co-corrole has been isolated in the form of the triphenylphosphine complex (VI). The attempts to obtain the N(21)-alkyl derivatives by alkylating Co(III)-corroles with alkylmagnesium bromide or alkyl-lithium were unsuccessful[30].

2. Alkylation of Metal Complexes of Octadehydrocorrins

The metal complexes of octadehydrocorrins also undergo the alkylation reaction. The alkylation of the nickel complexes of 1-methyloctadehydrocorrins by alkyl halides takes place in the 19-position with the formation of salts of the nickel complexes of 1,19-dialkyloctadehydrocorrins[18,21,38,40]. The CH_3, C_2H_5, n-C_3H_7, $CH_2=CHCH_2$, and $C_6H_5CH_2$ substituents have been introduced in this way into the 19-position[18]. Although the 19-position is not the usual reaction centre for electrophilic reactions, substituting in the 19-position in 1-methyloctadehydrocorrins causes the minimum interference with the conjugation of the system in the transition state. The alkylation of the nickel complexes of 1-ethoxycarbonyloctadehydrocorrins (XCI) also takes place in the angular position and leads to the formation of the nickel complexes of 19-alkyl-1-ethoxycarbonyloctadehydrocorrins (CVIIIa). The 19-methyl-,[59] alkyl-, and 19-(3,3-dimethylallyl)-derivatives[29] have been obtained in this way.



(XCI) (CVIIIa)

Since the cobalt complexes of 1-methyloctadehydrocorrins have not been isolated, their alkylation has been scarcely investigated. However, treatment of a solution of the cobalt complex of 1-methyloctadehydrocorrin with CH_3I in an inert gas atmosphere results in the formation of the 1,19-disubstituted derivative[2].

The methylation of the nickel complexes of 1,19-dimethyloctadehydrocorrins takes place in the *meso*-position but only to a slight extent. The methylation of the nickel complex of octa-alkyl-1,19-dimethyloctadehydrocorrin with CH_3I in the presence of $SnCl_4$ leads to the formation of the 5-methyl derivative in 6% yield [47].

Reductive methylation has been used to introduce the CH_3 group into the *meso*-position in the octadehydrocorrin macroring, which results in the formation of 10-methyloctadehydrocorrin (LVII).[60] The reductive methylation of salts of the nickel complexes of octadehydrocorrin (III) takes place as follows. On treatment with CH_3I in the presence of sodioanthracene in anhydrous THF in an inert gas atmosphere, the CH_3 group enters the 10-position with the simultaneous opening of the macroring and the formation of the nickel complex of undecamethylbiladiene (LVIII), the anthracene radical-anion functioning as an electron transferring agent in this reaction and participating in the formation of the anionic form $(III)^-$:

$$(III) + 2NaC_{14}H_{10} \rightarrow Na^+(III)^- + 2C_{14}H_{10} + NaI \ .$$

After the addition of CH_3I, the complex (LVIII) is formed:

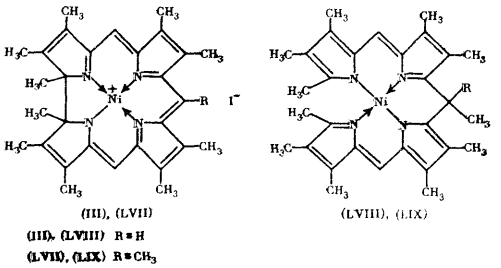
$$Na^+(III)^- + CH_3I \rightarrow (LVIII) + NaI \ .$$

The oxidation of this complex leads to the formation of the cyclic system (LVII):

$$(LVIII) + I_2 \rightarrow (LVII) + 2HI \ .$$

Repeated reductive methylation of undecamethyloctadehydrocorrin (LVII) again leads to the addition of the CH_3 group in the 10-position and ring opening with formation of

the complex (LIX), which does not cyclise into the nickel complex of octadehydrocorrin even under severe conditions[60] as a consequence of the presence of two geminal CH_3 groups[15].



(III), (LVII)

(III), (LVIII) R = H

(LVII), (LIX) R = CH_3

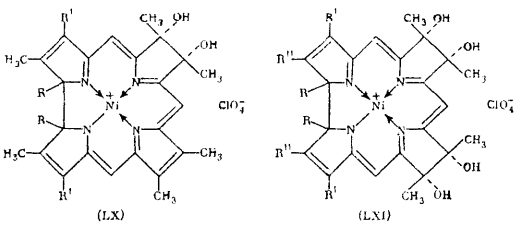
(LVIII), (LIX)

VI. REACTIONS INVOLVING THE β,β-DOUBLE BONDS

1. Hydroxylation of the Nickel Complexes of Octadehydrocorrins

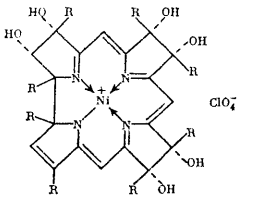
The octadehydrocorrin macroring contains 10 double bonds, 6 of which are involved in a system of conjugated C=C and C=N bonds constituting the chromophore, which is characteristic of both octadehydrocorrin and corrins, while the four β,β-double bonds are cross-conjugated in relation to the chromophore and are characteristic only of octadehydrocorrins.

One of the few reactions involving the β,β-double bonds is hydroxylation of the metal complexes of octadehydrocorrin on treatment with OsO_4.[61-64] The hydroxylation of the nickel complexes of decamethyl- and 1,19-diethoxycarbonyl-octamethyl-octadehydrocorrins[62,65] as well as the nickel and cobalt complexes of octadehydrocorrins containing the $C_6H_5CH_2O$ substituents in the 3- and 17-positions[63] results in the formation of a mixture of the corresponding 7,8-dihydroxy-derivatives (LX) and 7,8,12,13-tetrahydroxy-derivatives (LXI), i.e. the *B* and *C* rings are involved in the reaction in the first place. The composition of the mixture of compounds (LX) and (LXI) depends on the amount of OsO_4.[62] The reaction of OsO_4 with the nickel complexes of octadehydrocorrins containing the residues of acetic and propionic acids in the *A* and *D* rings proceeds analogously[64]. After the hydroxylation of octadehydrocorrins with free 2- and 18-positions, 2,3,7,8,12,13-hexahydroxycorrin (LXII) and 2,3,7,8,12,13,17,18-tetrahydroxycorrin (LXIII) were isolated in addition to the 7,8-diols and 7,8,12,13-tetraols[61,62,65]. As a consequence of the *trans*-disposition of the 1,19-substituents and the *cis*-hydroxylation, which takes place on either side of the plane of the octadehydrocorrin molecule, a mixture of diastereoisomeric racemates is formed.



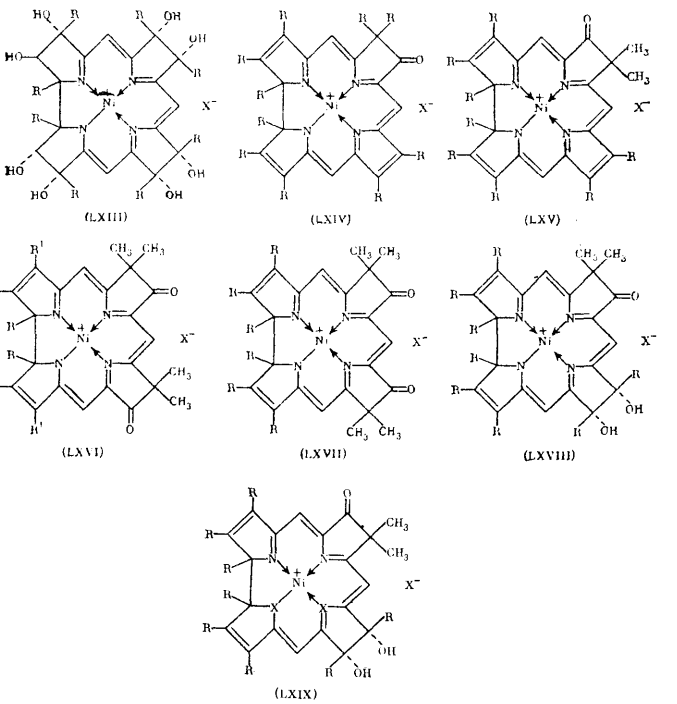
(LX)

(LXI)



(LXII)

On treatment with H_2SO_4, the β-dihydroxy-derivatives of corrinoids undergo the pinacol rearrangement, which leads to the formation of ketones containing the *gem*-dimethyl group. The diol (LX) is converted into a mixture of the two monomers (LXIV) and (LXV), which could not be separated[64]. After the pinacol rearrangement of the tetraol (LXI), the two diketones (LXVI) and (LXVII) were isolated. Brief treatment of tetradehydrocorrin having OH groups in the *A* and *D* rings with H_2SO_4 led to the isolation of only the hydroxyketone (LXVI, R′ = OH), in which the OH groups of the *A* and *D* ring are retained[63]. Of the three possible products of the rearrangement of each tetraol (LXI), it was possible to isolate only the diketones (LXVI) and (LXVII):[64]



(LXIII)

(LXIV)

(LXV)

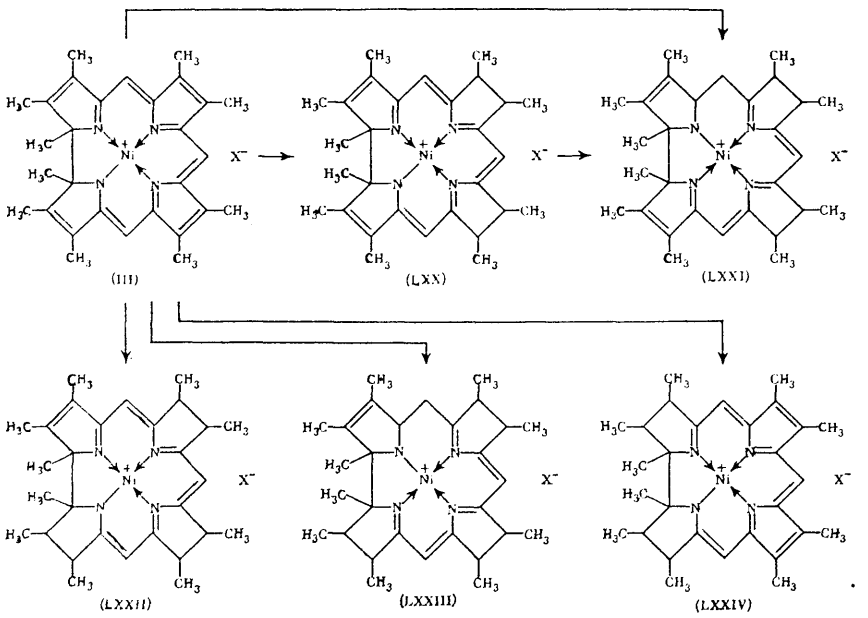
(LXVI)

(LXVII)

(LXVIII)

(LXIX)

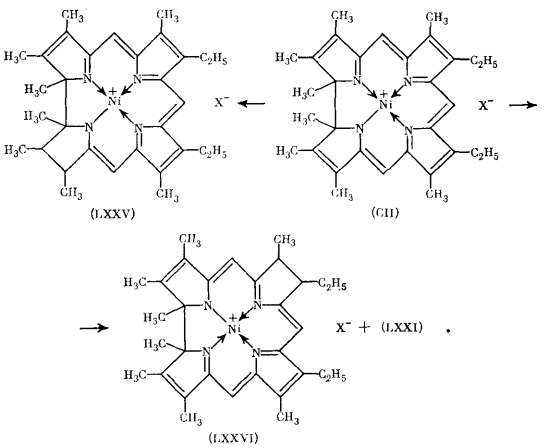
The products of the pinacol rearrangement, namely the mono- and di-ketones, can again undergo the hydroxylation reaction. After treatment with OsO_4, the mixture of the monoketones (LXIV) and (LXV) is converted into a mixture of the dihydroxyketones (LXVIII) and (LXIX). The amount of the dihydroxyketone (LXVIII) is three times greater than that of the dihydroxyketone (LXIX), apparently because the two CH_3 groups in the 8-position hinder the hydroxylation of the *C* ring[65]. The structures of the dihydroxyketones were confirmed by the products of their pinacol rearrangement: compound (LXVIII) is converted into a mixture of the diketones (LXVI) and (LXVII), while compound (LXIX) gives rise to only the diketone (LXVI).[61,62,65]



2. Hydrogenation of the Metal Complexes of Octadehydrocorrins

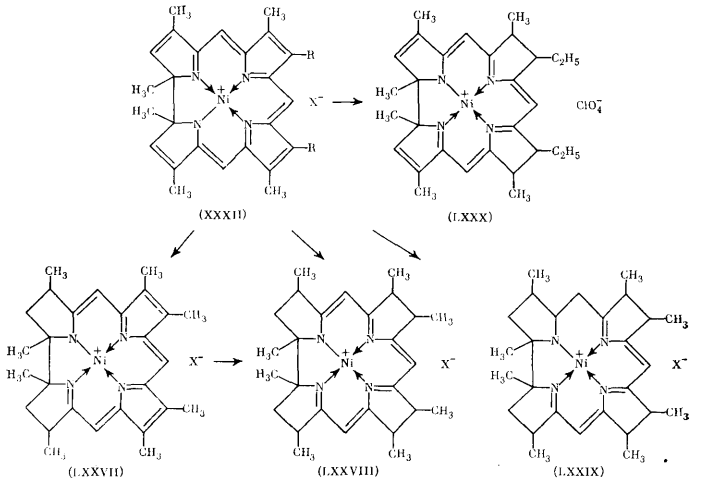
The second reaction involving the β,β-double bonds of the octadehydrocorrin macroring is hydrogenation, which leads under different conditions to a series of macrocylic compounds intermediate between corrins and octadehydrocorrins as regards degree of oxidation. The course of the hydrogenation reaction is greatly influenced by the β-substituents[66]. Hydrogenation of the metal complexes of octadehydrocorrins having alkyl groups in the 1-, 2-, 18-, and 19-positions involves in the first place the β,β-double bonds of the *B* and *C* rings. In the presence of Raney nickel at 100 °C and 100 atm, the nickel complex of decamethyloctadehydrocorrin is converted into the nickel complex of *AD*-tetradehydrocorrin(LXX),[66,67] which is also formed after reduction of the complex (III) in boiling acetic acid[67]. Further reduction of the *AD*-tetradehydrocorrin or the complex (III) over the 10% Pd/C catalyst (20 °C, 100 atm, 26 h) involves the addition of H_2 in the 4- and 5-positions of the macroring with formation of the complex (LXXI).[66] Vigorous hydrogenation of the complex (III) leads to the formation of *A*-hydrocorrin (LXXII) in which there is a β,β-double bond only in the *A* ring[67]. The most highly hydrogenated product is isocorrin (LXXIII), obtained on hydrogenation of the complex (III) over Raney nickel at 160 °C and 120 atm.[66]

The selective hydrogenation of the *B* and *C* rings in β-substituted octadehydrocorrins is a consequence of the steric hindrance generated by the substituents in the 1-, 2-, 18-, and 19-positions. However, the hydrogenation of the complex (III) over the 10% Pd/C catalyst in acetic acid leads to the reduction of the β,β-double bonds of the *A* and *D* rings and the formation of *BC*-tetradehydrocorrin (LXXIV).[66] The replacement of the CH_3 substituents in the 8- and 12-positions by the more bulky C_2H_5 groups changes the mode of reaction: the hydrogenation of the nickel complex of 8,12-diethyloctamethyloctadehydrocorrin (CII) over Raney nickel at 160 °C and 120 atm results in the formation of the nickel complex of *ABC*-hexadehydrocorrin (LXXV).[66] The hydrogenation of the octadehydrocorrin (CII) over the 5% $Pd/BaSO_4$ catalyst (20 °C, 100 atm, 5 days) leads to the formation of a mixture of the hexadehydrocorrin (LXXVI) and the complex (LXXI).[66] After the hydrogenation of the octadehydrocorrin (CII) or *AD*-tetradehydrocorrin under severe conditions, the didehydrocorrin (LXXII) was isolated[66]:



In the hydrogenation of the nickel complexes of octadehydrocorrins unsubstituted in the 2- and 18-positions [compound (XXXII)] and in the 2-, 3-, 17-, and 18-positions, H_2 adds in the first place to the β,β-double bonds of the *A* and *D* rings: the hydrogenation of the complex (XXXII) (20 °C, 50 atm) leads to the formation of a mixture of *BC*-tetradehydrocorrin (LXXVII) and the corrin (LXXVIII), while under more severe conditions the corrin (LXXVIII) was isolated with an admixture of the 4,5-dihydrocorrin (LXXIX). A mixture of corrin and 4,5-dihydrocorrin was also obtained on hydrogenation of the *BC*-tetradehydrocorrin (LXXVII).[66] The hydrogenation of the complex (XXXII) at 100 °C leads to the formation of *AD*-tetradehydrocorrin (LXXX),[2] while hydrogenation over Raney nickel at 100 °C and 100 atm yielded corrins[67,68]. The hydrogenation of the

nickel complex of 1,7,8,12,13,19-hexamethyloctadehydrocorrin over Raney nickel (20 °C, 50 atm) leads to the formation of the nickel complex of *BC*-tetradehydrocorrin[66].

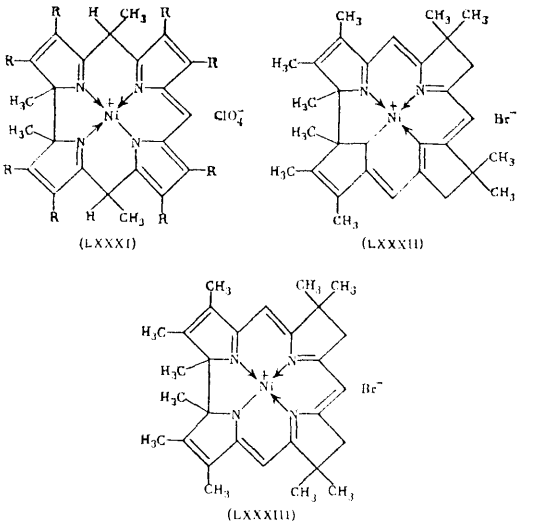


All the products of the hydrogenation of the nickel complexes of corrinoids containing 6 or 8 double bonds are capable of being dehydrogenated in the *B* and *C* rings in air and in the presence of basic catalysts[69]. The nickel complexes of corrins with unsubstituted 2-, and 18-positions[67,68] or 2-, 3-, 17-, and 18-positions[66,67] are converted into *BC*-tetradehydrocorrins, while the nickel complexes of *AD*-tetradehydrocorrins are converted into complexes of octadehydrocorrins[66,67]. The preferential dehydrogenation of the *B* and *C* rings is probably due to the steric hindrance in the region of the angular CH_3 groups or reflects the greatest acidity of the protons in the *B* and *C* rings compared with the acidity of those in the *A* and *D* rings.

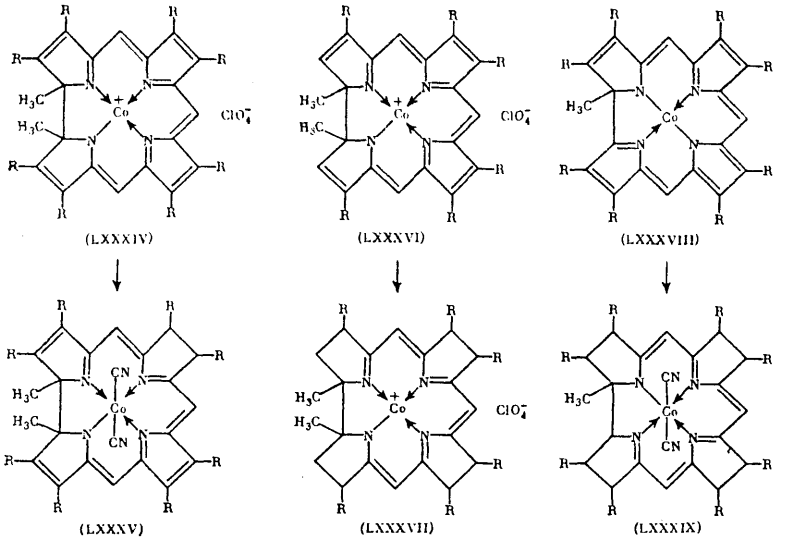
In the hydrogenation over platinum of the nickel complex of β-alkyloctadehydrocorrin containing CH_3 groups in the 5- and 15-positions, one mole of H_2 adds on and an unstable amorphous orange product (LXXXI),[15] whose electronic spectrum resembles that of the nickel complex of dipyrrolylmethene, is formed.

The hydrogenation of the nickel complex of 7,8,12,13-tetrahydroxyoctadehydrocorrin (LXI, R′ = H) over the Pd/C catalyst leads to a corrin, while the hydrogenation under the same conditions of the tetraol containing the $C_6H_5CH_2O$ substituents in the 3- and 17-positions results only in the elimination of the $C_6H_5CH_2$ groups.[63]

The hydrogenation of the diketones (LXVI) and (LXVII) over Raney nickel at 150 °C and 10 atm involves the CO groups and leads to the tetradehydrocorrins (LXXXII) and (LXXXIII).[65]

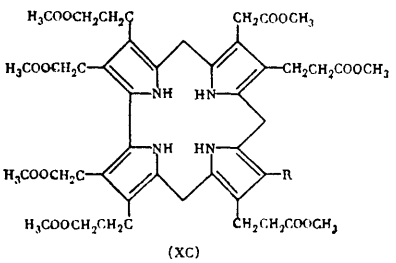


The hydrogenation of the cobalt complexes of octadehydrocorrin takes place analogously. The hydrogenation of the cobalt complex of octa-alkyl-1,19-dimethyloctadehydrocorrin (LXXIV) over Raney nickel at 100 °C and 100 atm results in the formation, after treatment with NaCN, of the dicyanocobalt complex of *AD*-tetradehydrocorrin (LXXXV),[15] which has also been obtained by the hydrogenation of the complex (LXXXIV) in methanol containing acetic acid over the 10% Pd/C catalyst at 80–82 °C and 85 atm.[70] The cobalt complexes of octadehydrocorrins (LXXXVI) with unsubstituted 2- and 18-position are converted into the corrins (LXXXVII) on hydrogenation at 175 °C and 100 atm,[38,68] while the



dicyanocobalt complex of corrin (LXXXIX), whose electronic spectrum is identical with that of cyanocobaltamin, was obtained in the form of an amorphous substance from the cobalt complex of 1-methyloctadehydrocorrin (LXXXVIII) under the same conditions after treating the hydrogenation product with CN^- ions[38].

When β-substituted octadehydrocorrins are hydrogenated, asymmetric carbon atoms are produced and the reaction products are mixtures of stereoisomers. The hydrogenation of the nickel complex of 1,19-dimethyloctadehydrocorrin (Raney nickel, 20 °C, and 25 atm or 160 °C and 100 atm), which has no β-substituents, led to another corrin complex[71,72]. The nickel complex of 1,19-dimethyloctadehydrocorrin is converted into crystalline corrin already at 20 °C and atmospheric H_2 pressure after 1 h.[72] The nickel complex of octadehydrocorrin acts itself as the catalyst of the hydrogenation proper: when a solution of the nickel complex of octadehydrocorrin is heated at 160 °C and 80–100 atm for 4 h without a catalyst, corrin is formed. The hydrogenation of the cobalt complex of 1,19-dimethyloctadehydrocorrin at 20 °C and 25 atm leads to a mixture of dicyanocobalt complexes of corrin and 4,5-dihydrocorrin after treatment of the product with CN^- ions; in the absence of treatment with cyanide ions, the perchlorate of the cobalt complex of corrin was isolated[72].



(XC)

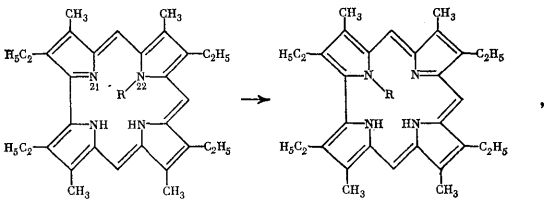
On hydrogenation over platinum, octa-alkylcorrole is converted into an unstable product, which is rapidly reoxidised in air to the initial corrole[3]. The hydrogenation of corroles containing the CH_3OOCCH_2 and $CH_3OOCCH_2CH_2$ groups in the β-positions over platinum oxide leads to colourless readily oxidisable crystalline corrologens (XC).[41]

VII. REARRANGEMENTS OF CORRINOIDS AND THEIR METAL COMPLEXES

The metal complexes of 1-alkyl- and 1,19-dialkyl-octadehydrocorrins as well as the metal complexes and the free bases of *N*-alkylcorroles undergo thermal rearrangements.

1. The Rearrangements of Corroles and Their Metal Complexes

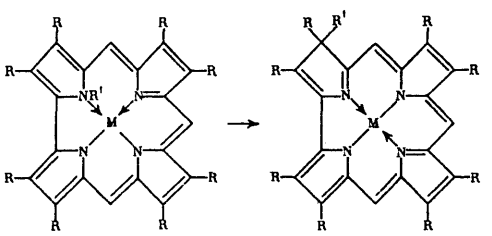
When *N*-alkylcorroles and their metal complexes are heated, the *N*-alkyl groups migrate to another N atom or to the 3-position in the macroring. N(22)-Methyl- and N(22)-allylcorroles (LI, a and b) are converted into N(21)-methyl and N(21)-allyl-corroles (XIX, a and b) on refluxing in toluene[19,21,28]. The thermal isomerisation of N(22)-allylcorrole in cumene[28] and the isomerisation of N(22)-3,3-dimethylallylcorrole (LIc) [19,28] showed that the migration proceeds via a free-radical mechanism.



(LI a–c) (XIX a–c)

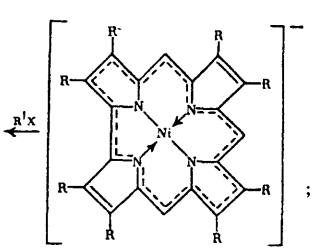
(a) R = CH_3; (b) R = $CH_2CH{=}CH_2$; (c) R = $CH_2CH{=}C(CH_3)_2$.

Heating of the nickel complexes of N(21)-alkylcorroles in chlorobenzene (130 °C, 90 min) leads to the formation of complexes of 3,3-dialkylcorroles (LIII).[9,21,23] The steric factor plays a major role in these reactions; migration of bulky alkyl substituents is the faster[23]. Thus N(21)-ethyl- and N(21)-propyl-corroles rearrange in boiling benzene, while the reaction of the Ni-corrole anion (XII) with $CH_2{=}CHCH_2Br$ or iso-C_4H_9I leads immediately to the nickel complex of the 3,3-disubstituted corrole[3,21,23]. The driving force of this arrangement is apparently the formation of a strong C–C σ-bond instead of the weak C–N σ-bond as well as the decrease of steric strain and the gain of the energy of stabilisation by the ligand field[21].



(V) (LIII)

M = Ni, Pd .

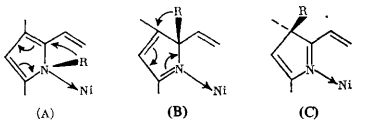


(XII)

The thermal arrangement of the metal complexes of *N*-alkylcorroles can proceed either via two [1,5]-sigmatropic shifts (A) → (B) → (C) or via the metal-[1,3]-sigmatropic shift (A) → (C). A choice between these two possibilities has not been made but preference has been given to the first possibility[9].

The rearrangement of the palladium complexes of N(21)-alkylcorroles takes place analogously; on heating in o-$C_6H_4Cl_2$, they are converted into complexes of 3,3-dialkylcorroles (LII).[27,28] The temperature of the rearrangements of the palladium complexes is higher than that of the nickel complexes probably as a consequence of the steric hindrance due to the large bulk of palladium.

The copper complexes of N(21)-ethylcorroles are converted into the complexes of *N*-unsubstituted corroles, while the complexes of N(22)-ethylcorroles are cleaved[28].

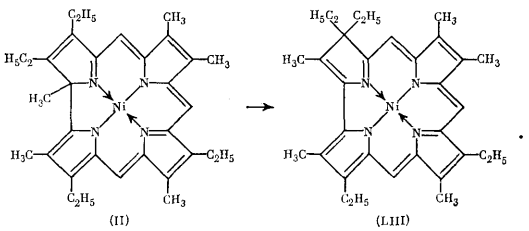


(A) (B) (C)

2. The Rearrangement of the Nickel Complexes of 1-Substituted Octadehydrocorrins

The thermal rearrangements of the metal complexes of 1-substituted and 1,19-disubstituted octadehydrocorrins take place with an alteration in the type of the tetrapyrrole macroring and the formation of more conjugated compounds.

On refluxing in o-$C_6H_4Cl_2$, the nickel(II) complexes of 1-methyloctadehydrocorrins are converted into the complexes of 3,3-dialkylcorroles (LIII).[18,21,29,56] The structure of the nickel complex of 2,2-dialkylcorrole was initially attributed to the thermal isomerisation product, since the nickel complex of 2-methylcorrole is formed in the case of 1-methyloctadehydrocorrin with an unsubstituted 2-position (XVI):[18,56]

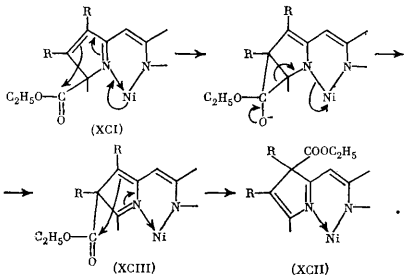


(II) (LIII)

However, it was found that the migration of the substituent from the 1-position takes place in two stages: initially to the 2-position with formation of 2,2-dialkylcorrole, which is followed by the shift of the substituent with the greater capacity for migration to the 3-position[21,29]. This sequence of reactions was demonstrated in the transformation of the nickel complex of 2,3,12,17-tetraethyl-1,7,8,13,18-pentamethyloctadehydrocorrin into the nickel complex of 3,3-diethylcorrole, whose formation is possible when 2-ethyl-2-methylcorrole is formed initially and then 3,3-diethylcorrole is produced as a consequence of the greater mobility of the ethyl group[29]. The migration of the angular CH_3 group from the 1-position to the 3-position can be regarded as a sigmatropic shift[73]. The capacity of substituents for migration varies in the sequence $CH_2{=}CHCH_2 > COOC_2H_5 > C_2H_5 > CH_3$.[21,29] The mechanism of the rearrangement of the nickel complexes of 1-substituted octadehydrocorrins was confirmed experimentally in the thermolysis of the nickel complex of 1-ethoxycarbonyloctadehydrocorrin (XCI), which is converted into the complex of 3-alkyl-3-ethoxycarbonylcorrole (XCII) on heating in boiling chlorobenzene, while on standing in the solid state (20 °C, 2 days) or in CH_2Cl_2 (12 h) in the dark it is converted into the complex (XCIII) containing the $COOC_2H_5$ group in the 2-position; the latter rearranges to the complex of 3,3-disubstituted corrole (XCII) on heating for 1 h in chlorobenzene[59].

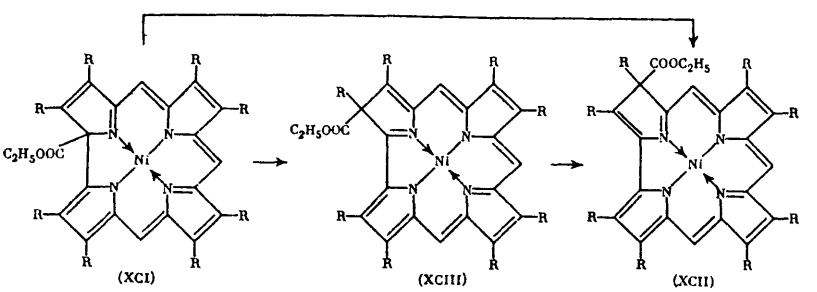
3. Rearrangements of the Metal Complexes of 1,19-Disubstituted Octadehydrocorrins

The metal complexes of 1,19-disubstituted octadehydrocorrins rearrange either into porphyrin complexes or into corrole complexes depending on the type of the angular substituents. The nickel complexes of 1,19-dialkyloctadehydrocorrins are converted into porphyrin complexes, while the nickel complexes of 1,19-diethoxycarbonyl- and 19-allyl-1-ethoxycarbonyl-octadehydrocorrins are converted into complexes of 3,3-disubstituted corroles. When the nickel complexes of octa-alkyl-1,19-diethoxycarbonyloctadehydrocorrins are heated in chlorobenzene, the complexes of 3-alkyl-3-ethoxycarbonylcorroles (XCII) are formed[20,56], the first stage involving the elimination of one angular $COOC_2H_5$ group and the formation of the nickel of 1-ethoxycarbonyloctadehydrocorrin (XCI), which was isolated when 1,19-diethoxycarbonyloctadehydrocorrin was treated cautiously with aqueous alkali. When the complex is heated in chlorobenzene, compound (XCII) is formed[29]. The migration of the ester group is either a [1,5]-sigmatropic shift analogous to the [1,5]-alkyl migration or the reaction mechanism involves the participation of the nickel atom and constitutes the sequence (XCI) → (XCIII) → (XCII).



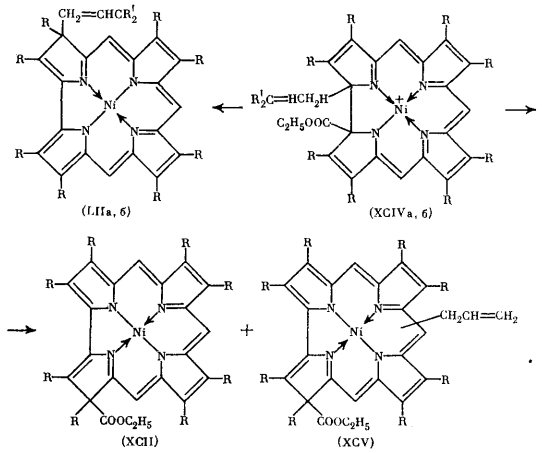
(XCI) (XCIII) (XCII)

The rearrangement of the nickel complex of octa-alkyl-19-allyl-1-ethoxycarbonyloctadehydrocorrin (XCIVa, R′ = H) takes place analogously; on treatment with NaOH, this compound is converted into the complex of 3-alkyl-3-allylcorrole (LIIa, R′ = H).[29] The rearrangement of the nickel complex of 19-ethoxycarbonyl-1-dimethylallyloctadehydrocorrin (XCIVb, R′ = CH_3) leads to the formation of the nickel complex of 3-ethyl-3-dimethylallylcorrole (LIIb. R′ = CH_3), i.e. takes place without the inversion of the

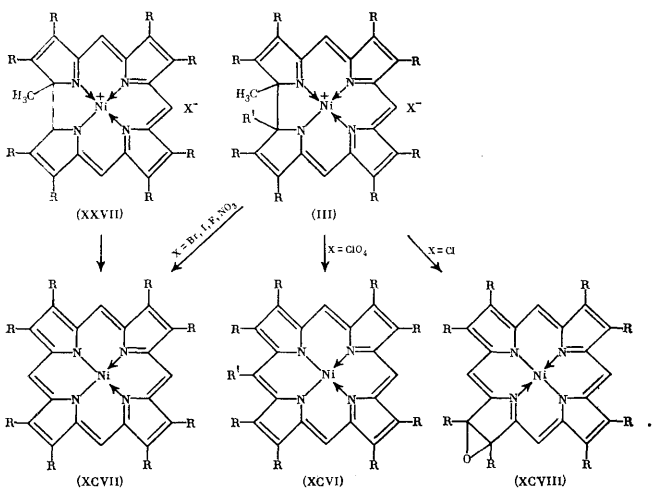


(XCI) (XCIII) (XCII)

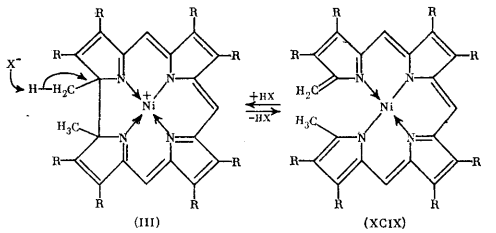
allyl substituent[42]. It is therefore probable that the allyl group migrates via two [1,5]-sigmatropic shifts C(1) → C(2) → C(3), as in the migration of the ester group. The thermal rearrangement of the nickel complex of 19-allyl-1-ethoxycarbonyloctadehydrocorrin (XCIVa) at 180 °C leads to the formation of a mixture of the complexes of 3-ethoxycarbonyl-3-methylcorrole (XCII) and the *meso*-allyl-3-ethoxycarbonylcorrole (XCV).[29]



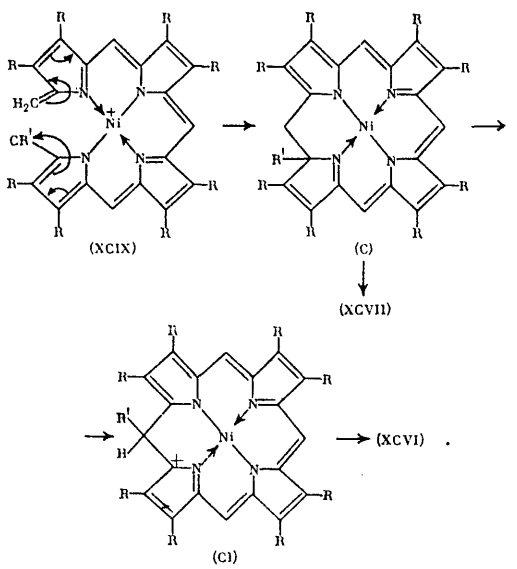
The thermal rearrangement of the salts of the nickel complexes of 1,19-dialkyloctadehydrocorrins take place with expansion of the macroring and consists in the conversion of octadehydrocorrins into porphyrins[21,24,43,74]. The pathway followed in this reaction depends on the nature of the anion: the perchlorates give rise to *meso*-alkylporphyrins (XCVI), while the iodides, bromides, fluorides, and nitrates produce the *meso*-unsubstituted porphyrins (XCVII); the third type of rearrangement is that of chlorides into 2,3-epoxy-5-methylchlorin (XCVIII).[43,74] The salts of the nickel complexes of 1-methyloctadehydrocorrins are converted into *meso*-unsubstituted porphyrins.



The first stage of the octadehydrocorrin–porphyrin rearrangement involves the elimination of a proton from one of the angular groups on attack by the anion, which acts as a base. This entails the dissociation of the C(1)–C(19) bond in the macroring of the type of the Hoffman elimination with formation of a neutral complex of bilatriene (XCIX).[24] The complex (XCIX), containing the benzylidene group instead of the methylene group, was isolated in the rearrangement of the bromide of the nickel complex of 19-benzyl-1-methyloctadehydrocorrin[74]. One of the angular groups, usually a methyl group, is a source of the fourth *meso*-carbon atom in the formation of the intermediate complex (C), which undergoes the following transformations: in the case of the I^-, Br^-, F^-, and NO_3^- anions, a second angular group is split off and the nickel complex of the *meso*-unsubstituted porphyrin is formed.



It has been shown that in the thermolysis of the iodide [of the nickel complex] of octa-alkyl-1,19-dimethyloctadehydrocorrin the angular CH_3 group is split off in the form of CH_3I, which suggests that the anion eliminates the angular group on nucleophilic attack[74]. In the case of the ClO_4^- anion, which is a weak nucleophile, the 19-alkyl group migrates and the *meso*-substituted porphyrin is formed. Since the ClO_4^- anion has oxidising properties, the rearrangement of the perchlorates apparently proceeds via the cationic form (CI), which is converted after oxidation into the porphyrin (XCVI).[74] In the thermolysis of the perchlorates of the nickel complexes of octadehydrocorrins containing the CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, $CH_2CH{=}CH_2$, and $COOC_2H_5$ groups in the 19-position, the substituents migrate without the isomerisation of the carbon skeleton with the exception of the allyl group, which is converted into the propenyl group[74]. Only the *meso*-alkylporphyrins are formed in the rearrangement of the perchlorates of the nickel complexes of 1,19-dialkyloctadehydrocorrins with unsubstituted 2- and 18-positions, i.e. there is no migration of the alkyl group to a neighbouring free β-position[74].



The thermolysis of the chlorides of the nickel complexes of 1,19-dimethyloctadehydrocorrins leads to the formation of complexes of 2,3-epoxy-5-methylchlorins (XCVIII) and *meso*-unsubstituted porphyrins, i.e. one angular CH_3 group migrates to the *meso*-position and the β,β-double bond of the neighbouring pyrrole ring is oxidised. Since the nickel complexes of porphyrins are insensitive to this type of oxidation by air, the substrate must be a non-aromatic product, for example, compound (XCIX) or the cyclic derivative (C).[43]

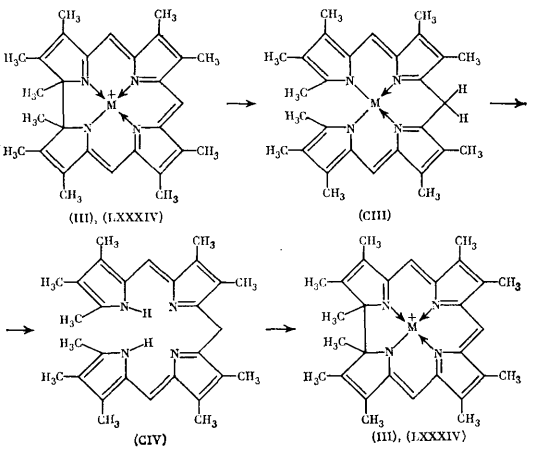
The presence of substituents in the *meso*-positions of 1,19-dialkyloctadehydrocorrins does not influence the rearrangement. For example, the iodides of the nickel complexes of octa-alkyl-5-cyano-1,19-dimethyloctadehydrocorrin and octa-alkyl-5,15-dicyano-1,19-dimethyloctadehydrocorrin are converted into the nickel complexes of the corresponding 5-cyano- and 5,15-dicyano-porphyrins on thermolysis[43].

The thermolysis of the cobalt complexes of octa-alkyl-1,19-dimethyloctadehydrocorrins leads to the formation of the corresponding cobalt complexes of porphyrins[75].

4. The Reductive Opening of the Macroring of the Metal Complexes of Octadehydrocorrins

The metal complexes of octadehydrocorrins are extremely stable. The cobalt and nickel atoms cannot be removed from these compounds without disrupting the macroring[75].

The interconversions of the nickel and cobalt complexes of the octadehydrocorrins (III) and (LXXXIV) have been achieved by treatment with reducing agents, which leads to the opening of the macroring between the C(1) and C(19) atoms with formation of the metal complexes of bilatrienes or the tautomeric biladienes, which are readily demetallated and can be recyclised to the metal complexes of octadehydrocorrins on treatment with $(CH_3COO)_2Ni$ or $(CH_3COO)_2Co$ in air.



The following mechanism for this migration has been proposed[79]: the metal complex of octadehydrocorrin, for example, the nickel complex (III), combines with two electrons under reductive conditions (in the presence of H_2S or $Na_2S_2O_4$) and is converted into a negatively charged complex, which, after the dissociation of the C(1)–C(19) bond, into the metal complex of 22,24-dihydrobilatriene and the latter is converted, after protonation at C(10), into a neutral complex of biladiene (CIII). On treatment with CF_3COOH, HCl, or even H_2S, the latter is demetallated and the resulting biladiene (CIV) can be reconverted into the metal complex of the octadehydrocorrin on treatment with nickel or cobalt acetate in the presence of atmospheric oxygen. The cobalt complexes of octadehydrocorrins are much more reactive than the corresponding nickel complexes; the opening of their rings takes place under very mild conditions (H_2S, room temperature)[76] and on treatment with HBr these compounds are converted into the monohydrobromides of bilatrienes-*abc*.[75]

The C(1)–C(19) bond is ruptured also on hydrogenation of the nickel complex of 3,17-benzyloxyoctadehydrocorrin over the 10% Pd/C catalyst, the resulting metal complex of biladiene recyclising in air at 20 °C.[63]

The principle of the reductive ring opening has been used to obtain the cobalt complex of 7,8-dihydroxy-, 7,8,12,13-tetrahydroxy-, 8.13-dioxo-, and 8,12-dioxo-decamethyloctadehydrocorrins, which could not be obtained by another procedure[76,77].

The stability of the nickel complexes of the tetrapyrrole macrorings with respect to reducing agents increases on successive saturation of the β,β-double bonds in the *B* and *C* rings:

$$(LXXXIV) < (III) < (LX) < (LXVI) = (LXVII) < (LXI) \quad .$$

The cobalt complexes are so labile that substitution on the periphery of the macroring does not play an appreciable role.

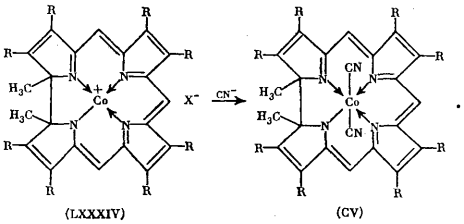
VIII. THE CHANGE IN THE OXIDATION AND COORDINATION STATES OF THE METALS IN THE METAL COMPLEXES OF CORROLES AND OCTADEHYDROCORRINS

1. The Redox Reactions of Corrinoid Compounds

The oxidation-reduction properties of vitamin B_{12} and its derivatives have been the subject of lively interest, since the oxidation state of the cobalt atom of cobalamin changes in the enzymatic B_{12}-dependent reaction[78].

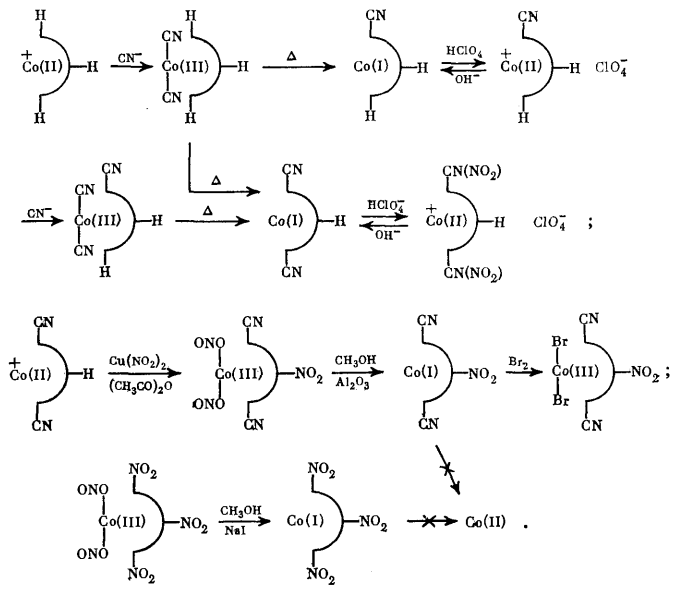
In recent years octadehydrocorrins have attracted attention as models of viatmin B_{12}. Ready interconversion of different oxidation states of cobalt takes place in the cobalt complexes of octadehydrocorrins (LXXXIV), in contrast to the stability of the bivalent nickel in the octadehydrocorrin complexes.

When the cobalt(II) complex of octa-alkyl-1,19-dimethyl-octadehydrocorrin is treated with a cyanide, the CN group does not enter the macroring. Instead a green diamagnetic dicyanide (CV) is formed, where two CN groups are located in the axial positions at the Co atom, which is oxidised to the tervalent state[15,63,75,79,80]. When cobalt(II) complexes of octadehydrocorrins are treated with $Cu(NO_3)_2$ in acetic anhydride, simultaneous nitration of the *meso*-positions of the macroring and the formation of a cobalt(III) complex with the ONO axial ligand take place; the *meso*-unsubstituted octadehydrocorrin is then converted into a mixture of 5,15(10)-dinitro- and 5,10,15-trinitro-octadehydrocorrins, while 5,15-dicyano-octadehydrocorrin is converted into 5,15-dicyano-10-nitro-octadehydrocorrin. On treatment with methanol, they are converted into salts of the cobalt(II) complexes of the corresponding octadehydrocorrins[75,79].



Cobalt(III) complexes of octadehydrocorrins can be obtained also from the cobalt(I) complexes. Treatment of the cobalt(I) complexes of 5,15-dicyano-10-nitro- and 5,10,15-trinitro-octadehydrocorrins with Br_2 leads to the formation of the dibromides of the cobalt(III) complexes of the corresponding octadehydrocorrins[75].

Cobalt(I) complexes of octadehydrocorrins are formed from both the cobalt(II) complexes[75] and from the cobalt(III) complexes[75,79]. When salts of the cobalt(II) complexes of monocyano- and dicyano-octadehydrocorrins were treated with alkali, neutral cobalt(I) complexes were obtained. This reaction is reversible; on treatment with $HClO_4$, the cobalt(I) complexes are converted into salts of the cobalt(II) complexes. The introduction of three electron-accepting substituents greatly stabilises the cobalt(I) complexes, which do not change on treatment with $HClO_4$. The thermolysis of the dicyanide of the cobalt(III) complex of the *meso*-unsubsituted octadehydrocorrin leads to the cobalt(I) complex of 5-cyano- and 5,15-dicyano-octadehydrocorrins, the latter being formed also on heating the dicyanide of the cobalt(III) complex of 5-cyano-octadehydrocorrin. The migration of the CN group from the Co atom to a C atom is probably an intermolecular process[75]. Treatment of the dinitrites of the cobalt(III) complexes of tri-*meso*-substituted octadehydrocorrins with NaI or Al_2O_3 in methanol also leads to the completion of the cobalt(I) complexes. The interconversions of the cobalt complexes of octadehydrocorrins can be represented schematically as follows:



The reduction of the cobalt(II) complexes of octadehydrocorrins on treatment with NaOH in aprotic solvents or with KOH in the form of a complex with a cyclic polyether also leads to the formation of cobalt(I) complexes, which are slowly reoxidised by atmospheric oxygen to the initial compounds[81]. It has been suggested[81] that an electron is transferred from the OH^- anion, which is unsolvated, to the cobalt(II) complex of octadehydrocorrin; in the reduction of the cobalt(II) complexes to the cobalt(I) complexes on treatment with $(C_2H_5)_3N$, the electron transfer from the amine to the cobalt(II) complex of octadehydrocorrin takes place via an outer-sphere mechanism. The reaction of the cobalt(II) complex of 1,19-diethoxycarbonyloctamethyloctadehydrocorrin (CVIIIb) with $NaBH_4$ in DMF also leads to a cobalt(I) complex[82]. The cobalt(I) complexes of octadehydrocorrins are stable, remaining unchanged in air for several hours. Their treatment with pyridine or triphenylphosphine does not alter the electronic spectrum[79]. Treatment of the cobalt(I) complexes with $FeCl_3$ or I_2 entails their instantaneous conversion into the cobalt(II) complexes[4,81].

The reduction of the nickel(II) and cobalt(II) complexes of octa-alkyl-1,19-diethoxycarbonyloctadehydrocorrins (CVIIIb) in THF has been studied with the aid of optical spectra and EPR.[14] The formation of one- and two-electron reduction products was observed in both cases. The product of the one-electron reduction of the nickel complex is a very stable free radical, formed on addition of one electron to the lowest unoccupied π orbital of the ligand. The first reduction potential of the initial cation in DMF (−0.30 V) indicates the stability of the radical and corresponds to one-electron reduction. The one-electron reduction of the cobalt(II) complex leads to the formation of a neutral cobalt(I) complex, i.e. in contrast to the nickel(II) complexes, the electron adds to the central metal ion, whose oxidation state changes. When reduced nickel and cobalt complexes of octadehydrocorrins are treated with oxidants (I_2, $FeCl_3$), the initial compounds are quantitatively regenerated[14].

Further reduction of the cobalt(I) complex of octadehydrocorrin and of the free radical of the nickel(II) complex also proceeds as a one-electron process, which leads in both cases to complexes of the bivalent metals with two additional electrons in the ligand π orbital. The oxidation of these substances in air results in the regeneration of approximately 90% of the products of the first reduction stage. Both nickel and cobalt complexes of octadehydrocorrins can be reduced further, but the compounds formed were not identified and the products of the preceding reduction stage cannot be regenerated on oxidation in air.

The reduction of the cobalt complexes of octadehydrocorrins constitutes a series in which the oxidation state of the central cobalt ion changes as follows: (II) → (I) → (II) with consecutive addition of one electron, and the final change from cobalt(I) to cobalt(II) must be a result of electron transfer from the cobalt(I) ion to the ligand together with competitive reduction of the ligand[14].

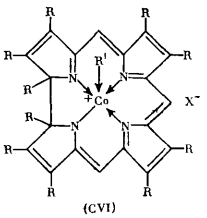
The electrolytic reduction of salts of the cobalt(II) complexes of 5,15-dicyano- and 5,15-dinitro-octadehydrocorrins at a platinum electrode leads to the formation of stable cobalt(I) complexes[73,79]. The reduction of the cobalt complexes of mono- and di-substituted octadehydrocorrins as well as unsubstituted octadehydrocorrins is a reversible one-electron process. The cobalt(I) complexes are stabilised with respect to oxidation in the presence of strong electron-accepting substituents in the macroring.

The reduction of the cobalt(III) complexes of corroles (XXI) with an Na film in THF *in vacuo* and also with $NaBH_4$ or $(C_4H_9)_4NOH$ in DMF leads to the formation of Co(II)-corrole anions (XII), which are reconverted in air into the initial cobalt(III) complexes of corroles[13,31]. The first reduction potential $E_{1/2} = -0.26$ eV. The enhancement of the electron-donating properties of the axial ligands hinders the reduction of the central cobalt ion[30]. When pyridine is added to solutions of the square-planar or pyramidal cobalt(III) complexes of corroles, $E_{1/2}$ becomes −0.54 eV in all cases as a consequence of the formation of the octahedral dipyridine complex[30]. According to other data[13], the potential of the reduction of Co(III)-corrole to the Co(II)-derivative is −0.34 eV in DMF and −0.47 eV in the presence of pyridine. All the redox processes are of the one-electron type and are

reversible[30], while the oxidation of the corrole bases is a quasi-reversible process[83].

2. The Coordination Properties of the Cobalt Atom in Complexes of Corrinoids

The central cobalt atom in the cobalt(II) complexes of octadehydrocorrins can be both tetracoordinate and pentacoordinate. The cobalt(II) complexes of octadehydrocorrins readily coordinate in the axial position one pyridine molecule[13] and also CH_3OH and DMF [13,14] with formation of pentacoordinate square-planar cobalt(II) complexes of octadehydrocorrin (CVI), [13,81] the unpaired electron being delocalised from the d_{z^2} orbital of the cobalt(II) atom over the coordinate bond between cobalt and the nitrogen atom of pyridine[13,82].

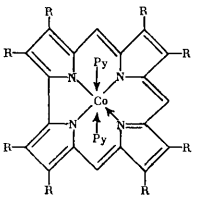


(CVI)

When pyridine and polyvinylpyridine are coordinated to the cobalt(II) complexes of 2,18-substituted octadehydrocorrin, the formation constants of the pentacoordinate complexes increase with enhancement of the electron-accepting properties of the β-substituents[84]. There is a linear relation between $\lg K$ for the coordination of pyridine and the σ_m constants of the β-substituents[84]. The constants of the coordination of substituted pyridines and aliphatic amines to the cobalt(II) complex of 8,12-diethyloctamethyloctadehydrocorrin have also been determined and correlations have been established between the coordination constants and the basicity of 4-substituted pyridines, on the one hand, and the coordination constants and the σ constants of the pyridine substituents, on the other[81]. The complexes of aliphatic amines and Co-octadehydrocorrins are less stable than the pyridine complexes. A mechanism has been proposed for the formation of these complexes, which consists in the amine giving up two electrons to the cobalt(II) complex in stages, the first electron being transferred to the cobalt atom via an outer-sphere mechanism and the resulting cobalt(I) complex and the electron-deficient amine combining to give a pentacoordinate cobalt(II) complex of octadehydrocorrin[81].

The coordination state of the cobalt(II) complexes of octadehydrocorrins depends on the nature of the anion[85]. The perchlorates and nitrates are tetracoordinate complexes, while the acetates and bromides are pentacoordinate. The nickel complexes of octadehydrocorrins are tetracoordinate in all the known cases and the nature of the anions does not affect this.

The cobalt(III) of corroles form both 1 : 1 and 1 : 2 adducts with pyridine and other amines[86]. The addition of an excess of pyridine to solutions of the square-planar or pyramidal complexes of corroles leads to the formation of the octahedral dipyridinecobalt(III) complexes of corroles (CVII), which are stable only in the presence of an excess of pyrine[30].



(CVII)

Correlations have been established between the formation constants of the penta- and hexa-coordinate cobalt(III) complexes of corroles and the basicity of the 4-substituted pyridines and between the constants of the coordination of 4-substituted pyridines to Co(III)-corroles and the σ constants of the pyridine substituents[86].

IX. REACTIONS OF SUBSTITUENTS IN THE CORRINOID MACRORINGS

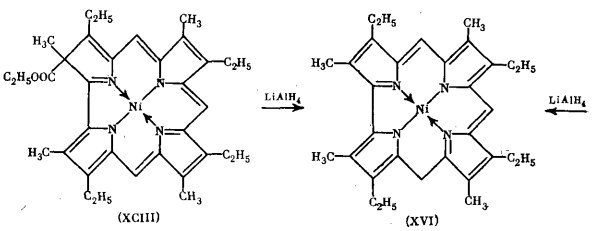
The reactions of substituents in the octadehydrocorrin macroring have been little investigated. The reactions of substituents in the 1- and 19-positions have been studied in greatest detail, since their removal leads to the formation of other types of tetrapyrrole macrorings.

When the nickel and cobalt complexes of 1,19-diethoxy carbonyloctadehydrocorrins are treated with alkaline agents, the ester is hydrolysed and the resulting carboxylic acids are carboxylated, while treatment with a solution of $(C_4H_9)_4$. .NOH in methanol yielded complexes of the tetrabutylammonium salt of 1-carboxyoctadehydrocorrin[14]. Rapid treatment of the nickel complex of 1,19-diethoxycarbonyloctadehydrocorrin (CVIIIb, R′ = $COOC_2H_5$) with a solution of NaOH in water[29] or methanol[59] leads to the nickel complex of 1-ethoxycarbonyl octadehydrocorrin.

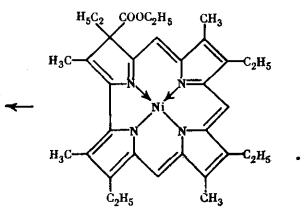
When the nickel complexes of 1-ethoxycarbonyl- and 1,19-diethoxycarbonyl-octadehydrocorrins (XCI) and (CVIIIb) are reduced with $LiAlH_4$, one ester group is eliminated and corrole and 1-ethoxycarbonyloctadehydrocorrin are formed respectively[59]. The nickel complex of 19-ethoxycarbonyl-1-methyloctadehydrocorrin (CVIIIa) is readily converted into the nickel complex of 1-methyloctadehydrocorrin on treatment with NaOH in methanol[29,40] or with sodium in alcohol[59].

The cobalt complexes are more reactive. When the cobalt complex of 1,19-diethoxycarbonyloctadehydrocorrin is treated with a solution of NaOH in methanol at 20 °C, the cobalt complex of corrole is formed[40].

Ester substituents at any saturated carbon atom are readily removed. When the nickel complexes of corroles, (XCII) and (XCIII), containing the $COOC_2H_5$ groups at C(3) and C(2) are reduced with $LiAlH_4$, they are both rapidly converted into the same corrole (XVI): [59]



(XCIII) (XVI)



(XCII)

The hydrogenation of the nickel complex of 3,17-dibenzyloxyoctamethyloctadehydrocorrin over the 10% Pd/C catalyst in alcohol at 20 °C leads to the formation of the nickel complexes of 17-benzyloxy-3-hydroxy- and 3,17-dihydroxyoctadehydrocorrins[63]. The oxidation of triphenylphosphinecobalt(III) complexes of octa-alkylcorroles with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone results in the formation of 3,17-diformyl derivatives[30]. Thermolysis of the nitrate of the nickel complex of decamethyloctadehydrocorrin probably involves the transformation of the CH_3 group in the 3-position into the CN group via the mechanism $-CH_3 \rightarrow -CH{=}NOH \rightarrow -CN$; the nitrosation is caused by the nitrous vapours formed on decomposition of the NO_3^- anion[74]. An analogous reaction occurs in the thermolysis of the nitrate of the nickel complex of octa-alkyl-1,19-diethoxycarbonyloctadehydrocorrin[29,56].

The metal complexes of octadehydrocorrins with propionic acid residues in the β-positions readily undergo reactions characteristic of carboxylic acids. They are esterified on refluxing in methanol in the presence of $HClO_4$.[87] The esterification of the CH_2CH_2COOH groups in the 8- and 12-positions, which are less sterically shielded, proceeds more readily than the esterification of the same groups in the 2- and 18-positions. The reactions of metal complexes of octadehydrocorrins containing the CH_2CH_2COOH groups with epoxyethane leads to the corresponding esters which are the products of the addition of one epoxyethane molecule[87].

Thus the metal complexes of octadehydrocorrins have unusual chemical properties, whose study makes a considerable contribution to the chemistry of complex compounds and tetrapyrrole macrocyclic compounds.

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Phosphorylation of Carbochain Polymers

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The methods for the chemical modification of carbochain polymers by various phosphorylating agents are examined. The possible ways of utilising macromolecular compounds with phosphorus-containing groups in the side chain are surveyed. The bibliography includes 186 references.

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I. INTRODUCTION

The polymer analogue reactions of macromolecular compounds constitute one of the most important methods for the introduction of new functional groups into polymer side chains[1]. One of the most promising versions of this method involves the phosphorylation of carbochain polymers. The interest in this procedure can be readily accounted for because the introduction of a phosphorus atom into the side chains of the macromolecules of various polymers makes it possible not only to improve important properties of the initial high-molecular-weight compounds, such as fire resistance, hydrophilic properties, and thermal stability, but also (depending on the type of phosphorus-containing functional groups introduced) to obtain polymeric materials capable of ion exchange and sorption of transition metal ions from solutions and to synthesise polymers with oxidation-reduction properties and biological activity. Virtually all the macromolecular compounds modified by various phosphorylating agents are produced in large amounts and some of the products are manufactured on an industrial scale[2].

Extensive experimental data have now accumulated on the phosphorylation of carbochain polymers but there are no publications in the literature which survey adequately questions associated with this problem. The available monographs and review publications[3-11] only partially fill the gap in the systematic description and survey of data concerning this branch of the chemistry of macromolecular compounds and the chemistry of phosphorus.

II. OXIDATIVE CHLOROPHOSPHORYLATION OF CARBOCHAIN POLYMERS

One of the effective methods of phosphorylating carbochain polymers involves their treatment by phosphorus halides and oxygen—the oxidative chlorophosphorylation of hydrocarbons. Phosphonyl chloride groups can then be introduced into the polyethylene side chain[12-17] in accordance with the mechanism[9-15]

$$\ldots -CH_2-CH_2-CH_2- \ldots + PCl_3 + {}^1/_2O_2 \rightarrow \ldots -CH_2CHCH_2- \ldots + HCl\ .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad POCl_2$$

The reaction is carried out at 60–80 °C, whereupon polyethylene forms a solution in phosphorus trichloride. The rate of phosphorylation is determined by the rate of dissolution of oxygen in the mixture. When air is used instead of oxygen, the above reaction proceeds at a lower rate. The derivatives obtained contain up to 16% of phosphorus. With increase of the degree of phosphorylation, the crystallinity of the product diminishes relative to the initial polyethylene[12]. Under analogous conditions, the $POCl_2$ functional groups have also been introduced into the polypropylene macromolecule[18-20]:

$$\ldots -CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}- \ldots + PCl_3 + {}^1/_2O_2 \rightarrow \ldots -CH_2-\overset{CH_3}{\underset{POCl_2}{C}}-CH_2-\underset{CH_3}{CH}- \ldots + HCl\ .$$

It has been suggested that the phosphonyl chloride groups are linked mainly to a tertiary carbon atom in the polymer chain. With increase of the degree of phosphorylation, the hardness and rigidity of the polymer decrease. The phosphorus content reaches 7% in the final product.

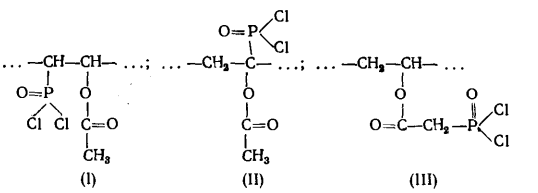
By treating the ethylene–propene copolymer with phosphorus trichloride and oxygen, Leonard et al.[21] and Weiss[22] obtained phosphorus-containing elastomers.

The heterogeneous oxidative chlorophosphorylation of polyethylene and ethylene–propene copolymers has also been investigated[23-29]. When thin films of polyethylene are treated with phosphorus trichloride vapour and oxygen, reactions of first order with respect to phosphorus trichloride and with 0.5 order with respect to oxygen take place. Phosphorylation takes place preferentially in the amorphous phase of the polymer.

Depending on the structure of the polyolefin chains, various reaction centres participate in the process. For branched polymers, such as high-pressure polyethylene and ethylene–propene copolymers, the main reaction centres are the hydrogen atoms at tertiary carbon atoms.

The phosphonyl chloride groups in polyolefins are highly reactive and undergo hydrolysis, alcoholysis and phenolysis and also interact with amines and metal salts. The hydrolysis of chlorophosphorylated polyolefins leads to the corresponding polymeric phosphonic acids[12].

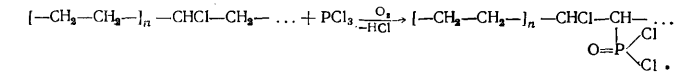
The oxidative chlorophosphorylation of poly(vinyl acetate), which resulted in the formation of copolymers containing units with different structures, has been investigated[30]:



(I) (II) (III)

It was suggested[30] that phosphorus enters mainly the polymer chain with formation of fragments (I) and (II).

It has been shown[31-33] that an analogous reaction takes place also when chlorinated polyolefins are used. For chlorinated polyethylene, this can be represented schematically in the following manner:



The phosphorus content in chlorinated polyethylene and atactic polypropylene increases with decrease of the chlorine content in the initial polymers and reaches 7.8 and 11.4% respectively.

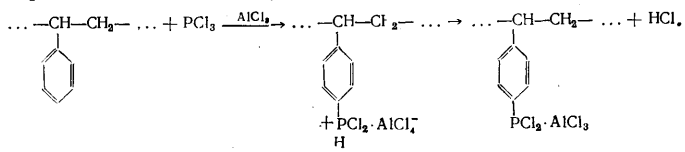
In a number of instances alkyl- and aryl-dichlorophosphines were used in the reaction instead of phosphorus trichloride[34-36]. This yielded polymers containing in the side chain groups characteristic of derivatives of dialkyl- or alkylaryl-phosphinic acids.

It is noteworthy that polyisobutylene, poly(methyl methacrylate), and polystyrene are degraded on phosphorylation, the final degradation product containing an insignificant amount of phosphorus[12]. A number of workers[37,38] believe that the oxidative phosphorylation can be classified as a process proceeding via a free-radical mechanism.

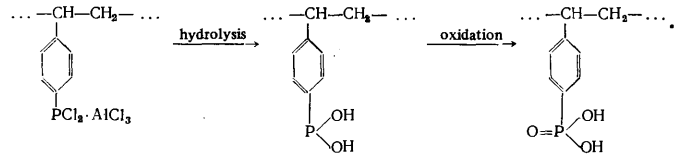
III. PHOSPHORYLATION VIA THE FRIEDEL–CRAFTS AND CLAY–KINNEAR–PERREN REACTIONS

A considerable proportion of the publications of the phosphorylation of carbochain polymers are associated with the employment of the Friedel–Crafts reaction. The phosphorylation of the copolymers of styrene with aromatic divinyl compounds has been studied in greatest detail[39-47]. Aluminium trichloride, titanium tetrachloride, tin tetrachloride, and zinc chloride have been recommended as catalysts. Aluminium trichloride has been used in most investigations, although it has been shown[48] that a more active catalyst, namely aluminium tribromide, would be more effective by increasing the degree of phosphorylation and reducing the reaction temperature.

The mechanism of the phosphorylation reaction can be represented schematically as follows:



The complex of the dichloride of polystyrylphosphonic acid with aluminium trichloride can subsequently hydrolyse and undergo consecutive oxidation reactions:

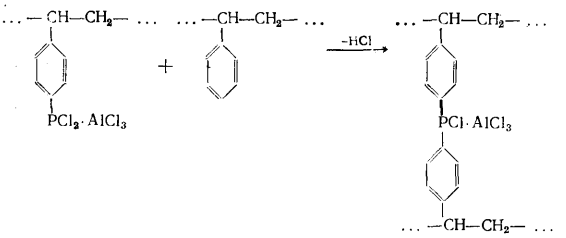


Nitric acid, SO_2Cl_2, and $SO_2–Cl_2$ and $Cl_2–P_2O_5$ mixtures, as well as other reagents are used as oxidants.

The interaction of cross-linked polystyrene with phosphorus trichloride followed by treatment of the resulting polystyrylphosphonic acid dichloride with a Grignard reagent led to the synthesis of monofunctional cation-exchange resins[50]. It has been stated that the substitution of two chlorine atoms in polystyrylphosphonic acid dichloride takes place stepwise as a result of steric hindrance. Under severe conditions, 85% of chlorine can be substituted to give the disubstituted derivative when ethylmagnesium bromide is used. Depending on the structure of the Grignard reagent, the degree of conversion decreases from 54 to 35% in the following sequence of substituents: $C_2H_5 > C_3H_7 > C_4H_9 > CH_3$.[51]

A detailed study of the influence of the reaction conditions on the degree of conversion of styrene–divinylbenzene copolymers[42] established that the latter depends on a series of parameters: the amount of aluminium trichloride and phosphorus trichloride, the reaction time, the degree of cross-linking of the copolymers, and their porosity.

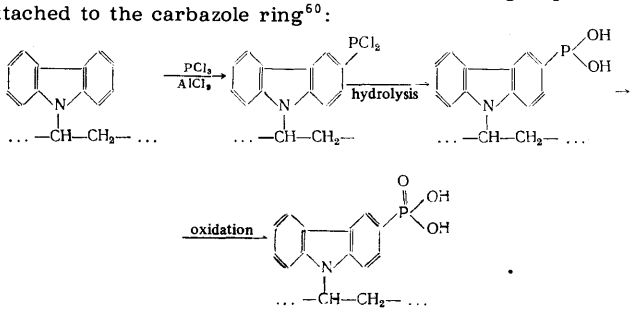
It has been noted that the macromolecules are cross-linked under the reaction conditions[49]:



The study of the kinetics of the phosphorylation of styrene–divinylbenzene copolymers established[45] that the principal rate-limiting stage is diffusion of the phosphorylating agent through the film of liquid adjoining the surface of the grain. The diffusion of the phosphorylating agent within the copolymer grains as well as its concentration in the swollen copolymer can also have a definite influence on the rate of phosphorylation. The conclusion that the phosphorylation process has an external diffusion mechanism is consistent with data[47] according to which the phosphorylation front migrates from the surface to the centre of the grain and the degree of phosphorylation depends on the depth to which the phosphorylating agent penetrates into the copolymers. With increase of the degree of cross-linking of the copolymers, the rate of reaction falls, but, for copolymers with a macroporous structure, obtained in the presence of an inert solvent, the rate of reaction increases sharply[52,53].

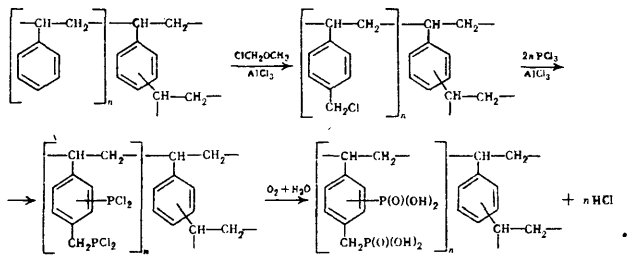
The phosphorylation of polystyrene grafted to polyethylene or polypropylene films has been achieved in a number of studies[54,55]. The phosphorylation was carried out at 40 to 65 °C by treatment with phosphorus trichloride in the presence of aluminium trichloride. On subsequent hydrolysis and oxidation with nitric acid, ion-exchange membranes with satisfactory electrochemical characteristics were obtained.

Modified copolymers with ion-exchange properties, a good mechanical strength, and an increased porosity and thermal stability have been obtained by the phosphorylation of macroporous ternary copolymers of styrene, divinylbenzene (1 to 20%), and acrylonitrile or ethyl, methyl, or butyl acrylate with phosphorus trichloride in the presence of aluminium trichloride[56-59]. The simultaneous treatment of poly-*N*-vinylcarbazole with phosphorus trichloride and aluminium trichloride yielded a product with the phosphonic acid group attached to the carbazole ring[60]:



The interaction was carried out in ethyl chloride with molar ratios polyvinylcarbazole : catalyst-phosphorylating agent of 1 : 2.5 : 10 in the temperature range 20–140 °C. Among phosphorylating agents, PCl_3 and PBr_3 proved to be the most effective and aluminium trichloride was the best catalyst. The degree of phosphorylation increased with temperature and reached a maximum (11.4% of phosphorus) at 76 °C (phosphorus trichloride) and 140 °C (phosphorus tribromide). The phosphorylated poly-*N*-vinylcarbazole has ion-exchange properties and does not dissolve in the usual organic solvents.

Polymers with phosphonic acid groups in the side chain have been obtained by treating chloromethylated vinyl derivative–aromatic compound copolymers with phosphorus trichloride in the presence of $AlCl_3$ in accordance with the scheme[61]



In this case substitution can take place via the Friedel–Crafts reaction in the benzene ring or via the Clay–Kinnear–Perren reaction in the chloromethyl group. Thus it has been suggested[62,63] that both reactions take place. Studies by Kinnear and Perren[64] showed that, when benzyl chloride interacts with PCl_3 and $AlCl_3$, phosphorylation takes place either in the chloromethyl group or in the aromatic ring, while simultaneous introduction of two phosphonic acid groups into the same benzene ring is unlikely.

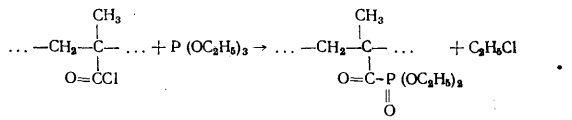
The phosphorylation of the chloromethylated styrene–divinylbenzene copolymer gives rise to lower degrees of conversion, compared with the phosphorylation of the non-chloromethylated copolymer, which can be explained by the greater ability for swelling of the latter in phosphorus trichloride[33].

Phosphonic acid cation-exchange resins can be obtained by the chloromethylation of condensed aromatic petroleum processing products followed by their phosphorylation with phosphorus trichloride in the presence of Friedel–Crafts catalysts and oxidation[65]. In terms of their activity, the catalysts can be arranged in the sequence $SnCl_4 > FeCl_3 > AlBr_3 > AlCl_3 > ZnCl_2$. The maximum degree of phosphorylation is attained when the ratio of the chloromethylated asphaltide to PCl_3 or $SnCl_4$ is 1 : 10, at a temperature of 35 to 60 °C, and for a process time ranging from 1 to 2 h. By virtue of their structure, which resembles that of graphite, they withstand more effectively the effects of small and large doses of γ-radiation compared with phosphonic acid cation-exchange resins based on styrene–divinylbenzene copolymers.

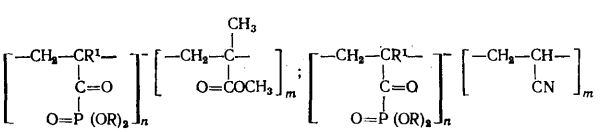
Nitrogen- and phosphorus-containing polymers with ion-exchange properties have been synthesised by polymer analogue reactions of the copolymers of styrene with divinyl compounds[66]. The initial and chloromethylated macronetwork copolymers of styrene and divinyl compounds were phosphorylated with phosphorus trichloride in the presence of $AlCl_3$. The divinyl compounds employed were ethylene-, hexamethylene-, and decamethylene-dimethacrylamides, dimethacrylate esters of di(hydroxyphenyl)sulphone and di(hydroxyphenyl)sulphoxide, and the dimethacrylamides derived from *m*-phenylenediamine, di(aminophenyl)ether, di(aminophenyl)methane, and di(aminophenyl)sulphide. In the synthesis of nitrogen- and phosphorus-containing amphoteric ion-exchange resins, the unsubstituted CH_2Cl groups in the partially phosphorylated chloromethylated copolymer were aminated with various isomers of pyridinedicarboxylic acids and their nitriles in dimethylformamide at 100 °C.[67] The presence of amide, ester, sulphoxide, sulphide, pyridinecarboxylic acid, and nitrile groups promoted an increase of the selectivity of the ion-exchange resins in relation to the sorbed ions.

IV. PHOSPHORYLATION OF CARBOCHAIN POLYMERS WITH THE AID OF THE ARBUZOV REARRANGEMENT

In one of the first studies of the Arbuzov rearrangement of macromolecular compounds, poly(vinyl chloroacetate), poly-α-chloroacrylate, poly(vinyl chloride), and the polymeric acrylic and methacrylic acid chlorides were used as the polymeric matrices[68]. The reaction was carried out in solution in dioxane at 100–150 °C using polymeric methacrylic acid chloride; it took place in accordance with the mechanism



When the chlorine atom is linked directly to a carbon atom of the main chain of the macromolecule, the degree of phosphorylation is insignificant. Best results were obtained in the reaction of triethyl phosphite with poly(vinyl chloroacetate). The resulting polymers were elastic and hygroscopic, did not support combustion, were resistant to acids, and exhibited an effective adhesion to glass. Polymers with analogous properties have been obtained by the reaction of triethyl phosphite with the copolymers of acryloyl or methacryloyl chloride and methyl methacrylate or acrylonitrile[69]:



Phosphorus-containing vinyl copolymers have been synthesised by the reaction of phosphonate esters with halogenomethyl groups in the copolymer and subsequent hydrolysis of the ester groups. The product had ion-exchange properties[70]. A cation-exchange resin has also been obtained by treating halogenomethylated copolymers of mono- and polyfunctional compounds with triethyl or trimethyl phosphite[71].

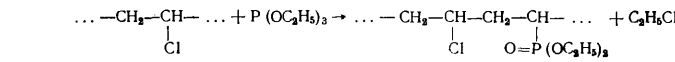
In order to improve the stability and non-combustibility of vinyl chloride polymers and copolymers, it has been suggested that they be treated with trialkyl phosphites[72,73]. The introduction of phosphonoethyl groups into the side chain of the copolymer of vinyl chloride with acrylonitrile is accompanied by an increase of its thermal stability and resistance to acids and organic solvents with retention of its non-combustibility.

Phosphorus-containing polymers with improved technological properties and strength parameters have been obtained by the reaction of trimethyl phosphite with chlorosulphonated polyethylene[74].

Several studies have been devoted to the reaction of poly(vinyl chloride) with mixed alkyl(aryl)phosphites[75–77]. According to the authors of these investigations, the reaction is accompanied by the Arbuzov rearrangement, which entails the appearance of phosphorylated units in the initial polymer. In the course of modification at 200 °C, the dehydrochlorination of the polymer with formation of polyconjugated double bonds was observed together with the main

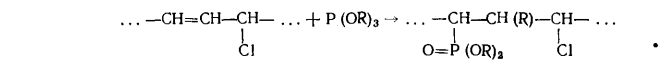
reaction. The specimens acquire a colour as a consequence of such modification.

The interaction of triethyl phosphite with poly(vinyl chloride) at 80–200 °C via the mechanism

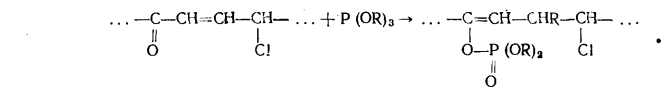


has been investigated[77]. The reaction was followed from the change in the chlorine and phosphorus contents in the final product. The polymers were amorphous powders soluble in organic solvents. At reaction temperatures up to 180 °C, there is no degradation of the polymer but on further increase of temperature a three-dimensional structure is formed.

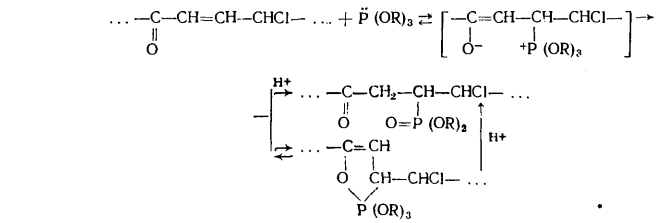
A detailed study of the mechanism of the interaction of poly(vinyl chloride) with trialkyl phosphites showed[79] that the hypothesis that phosphorus-containing compounds add to the double bond in poly(vinyl chloride) [78] is incorrect:



Thus the interaction of tributyl phosphite with 4-chloropent-2-ene does not entail the reaction with inner β-chloroallyl groups. The main process is the dehydrochlorination of 4-chloropent-2-ene. If the hydrogen chloride evolved in this process is not bound, tributyl phosphite is dealkylated with formation of dibutylphosphorus acid[79]. Data on the ozonolysis of poly(vinyl chloride) subjected to a preliminary treatment with a phosphorus-containing compound[81] indicate the absence of unsaturated C=C bonds in the main polymer chain and therefore cast doubt on the probability of the reaction of trialkyl phosphites with the carbonyl–allyl groups of macromolecules via the Perkow mechanism to form unsaturated phosphites[80]:



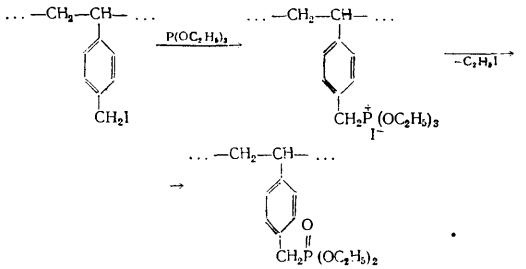
This effect may be attributed to the nucleophilic addition reaction in the presence of proton donors under the conditions of the stabilisation of poly(vinyl chloride) by organic phosphites involving attack by the latter on the β-carbon atom of the conjugated system of the carbonylallyl group followed by the protonation of the dipolar ion and the formation of a stable ketophosphonate[81]. Thus the reaction of organic phosphites with poly(vinyl chloride) under comparatively mild conditions leads to the quantitative opening of the inner unsaturated C=C bonds present in the polymer macromolecules with formation of single C–C bonds, which is due to the interaction of organic phosphites with the carbonylallyl groups of the polymer via the mechanism[82]



The occurrence of this interaction has been confirmed by the method of the competing reactions of trialkyl, alkyl, and aryl phosphites with a 1:1 mixture of methyl vinyl ketone (a model of the carbonylallyl group) and 4-chloropent-2-ene (a model of the β-chloroallyl group). Organic phosphites react selectively with methyl vinyl ketone, while 4-chloropent-2-ene is recovered unchanged from the reaction (apart from its dehydrochlorination products).[79]

Chloromethylated polystyrene and its copolymer with vinylidene chloride as well as poly(2,6-dimethyl-1,4-phenylene oxide), containing bromine in the side chain or in the benzene ring, are phosphorylated by triethyl phosphite (on refluxing in the presence of diethylmethanol) with formation of non-cross-linked polymers having phosphonate side groups[83]. The polyphosphonates are hygroscopic; the adsorbed water, whose amount increases with increase of the phosphorus content, influences the glass points of the polymers. The polyphosphonates can be combined with a large number of polymeric systems and may form "true" polymer alloys with acetylcellulose.

Iodomethylated derivatives of polystyrene are more readily phosphorylated by organic phosphites[84,85]:



At a temperature above 70 °C, the Arbuzov rearrangement with participation of macromolecules is accompanied by the isomerisation of triethyl phosphite under the influence of the ethyl iodide evolved in the reaction. It has been shown[84] that the rate constants for the Arbuzov rearrangement of triethyl phosphite in the presence of iodomethylated polystyrene decrease in the course of the reaction and that the apparent activation energy has different values at high and low temperatures.

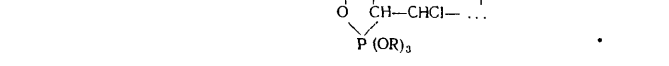
Products containing phosphonate groups in the side chain have been obtained by treating hydroxystyrene polymers with a phosphinate ester[86].

Dialkoxyphosphonomethylpolystyrenes have been obtained by the reaction of chloromethylpolystyrene with mixed alkyl phosphites having the general formula $(RO)_2POR^1$ (where $R = C_{3-7}$ alkyl and R^1 = methyl or ethyl) at 20–30 °C for 5–24 h and then at 170–190 °C for 10–20 h.[87]

Insoluble polymers containing polyalkylphosphonium groups in the side chain have been obtained by the reaction of PR_3 with diene, olefin, and alkylhalogeno-olefin polymers[88].

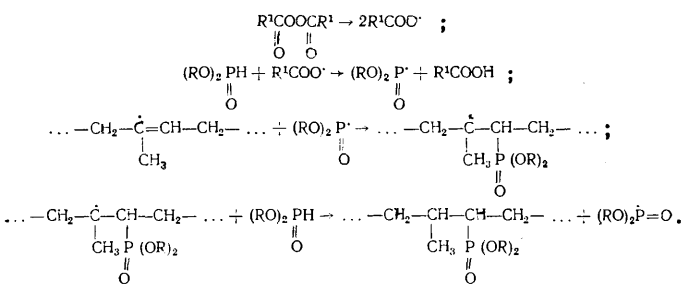
V. ADDITION OF PHOSPHORUS-CONTAINING COMPOUNDS WITH A MOBILE HYDROGEN ATOM TO UNSATURATED BONDS IN MACROMOLECULES

The addition of partially esterified phosphorus acids, initially investigated in relation to individual unsaturated compounds[89], was subsequently studied also in relation to polymers. The reaction was achieved for natural rubber by treatment of the latter with dialkyl phosphites[90] and somewhat later also for isoprene rubber[91]:



Investigation showed that, when various dialkyl phosphites are allowed to interact with natural rubber in the presence of benzoyl peroxide, it is possible to introduce up to 9–10% of phosphorus into the rubber, which corresponds to the addition of dialkyl phosphites to 60% of all the double bonds in the rubber. The vulcanised specimens obtained have reduced combustibility. With increase of the length of the

alkyl group in dialkylphosphorous acids, the content of the bound phosphorus in the polymer falls. A possible mechanism of such addition of dialkyl phosphites can be represented by the following scheme:

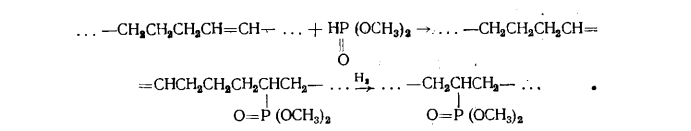


The polymers obtained do not dissolve in organic solvents and merely swell in them, which is apparently associated with the cross-linking resulting from the recombination of macroradicals.

The possibility of the addition of dialkyl phosphites to a dehydrochlorinated vinyl chloride–acrylonitrile copolymer has been demonstrated[92]. However, the phosphorus content in the final product was small (1.6 wt.%).

A method has been proposed for the synthesis of a phosphorus-containing polyallene by treating polyallene with dialkyl phosphites in the presence of organic peroxides as a result of irradiation with γ-rays at 20–140 °C.[93] The interaction of diorganophosphites with the product of the esterification of poly(vinyl alcohol) with the chloride of cinnamic acid has been investigated[94] and the influence of the nature of the initiator on the structure of the polymers obtained has been demonstrated. Structure formation was observed for peroxy-compounds, while in the presence of azobisisobutyronitrile the formation of a three-dimensional network was not observed. An increase of temperature to 120 °C increases the degree of phosphorylation but the final product ceases to be soluble. The introduction of phosphono-groups plasticises the initial polymer, reduces the softening temperature by 40–65 °C, increases the intrinsic viscosity, and imparts self-extinguishing properties to the polymer.

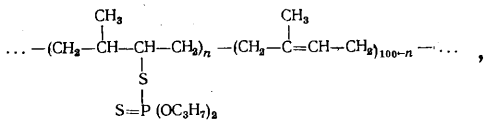
Phosphorylated derivatives of polycyclopentene containing 5–10 mole % of dimethylphosphonate groups have been obtained by the addition (initiated by peroxy-compounds) of dimethyl phosphite to the double bonds of polycyclopentene containing 82% of *trans*-double bonds, 17% of *cis*-double bonds, and 1% of vinyl side groups at 85–90 °C in solution in toluene with subsequent hydrogenation of the residual unsaturated bonds by toluene-*p*-sulphohydrazide at 145 °C:[95]



Dehydrated poly(vinyl alcohol) fibre containing 32–90% of double bonds is phosphorylated by dialkyl phosphites via the addition of the latter to the double bonds[96].

Phosphorylated raw rubbers for technical rubber articles have been obtained by the interaction of unsaturated raw rubbers in the form of aqueous latexes, stabilised by hydroxyethylated alkylphenols or higher alcohols, with dialkyl phosphites at 80–90 °C in the presence of radical initiators[97].

The reaction of *cis*-1,4-polyisopropene with di-isopropylphosphorodithioic acid in the presence of a catalyst led to the synthesis of a phosphorus-containing polymer having the structure[98]

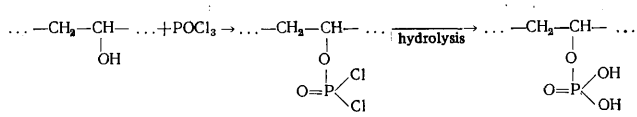


where $n = 5–63$. The polymer contains 0.7–6.9 wt.% of phosphorus and 0.9–16.6 wt.% of sulphur. The addition of certain other esters of dialkylphosphorodithioic acids to unsaturated elastomers has been carried out under analogous conditions[99,100]. The reaction takes place readily in the presence of benzoyl peroxide or isopropylphenyl hydroperoxide. The products contain 0.3–8 wt.% of phosphorus and 0.5–20% of sulphur and are readily soluble in organic solvents.

Phosphorus acids have been used in some investigations[101–104] as phosphorylating agents for carbochain polymers. Thus a phosphorus-containing polyallene has been obtained by treating polyallene with hypophosphorous acid in the presence of radical initiators in an inert gas atmosphere[103]. The final product contains 11 wt.% of phosphorus and is of interest for the formation of fire-resistant polymeric materials. Hypophosphorus acid proved to be the best phosphorylating agent in the hydrophosphorylation of polymers containing allyl groups in the side chain[101]. Polymers containing from 4 to 11% of phosphorus and having self-extinguishing properties have been obtained by this reaction.

VI. OTHER METHODS

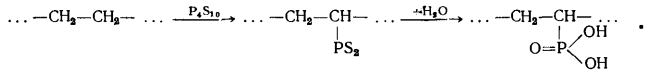
Phosphoryl chloride is an effective phosphorylating agent for hydroxyl-containing polymers. Phosphorylated derivatives of poly(vinyl alcohol) have been obtained by reaction with $POCl_3$.[105–107] After phosphorylation, the polymer loses its solubility in water and the phosphorus content in the final product reaches 14.7%. The potentiometric titration curve for the hydrolysed product has the form characteristic of dibasic acids. The reaction proceeds via the mechanism



The degree of conversion of the poly(vinyl alcohol) units in the phosphorylation reaction reaches 30–35%, which corresponds to one phosphoric acid group for each three hydroxy-groups in the polymer.

A series of ion-exchange materials have been synthesised by treating with phosphoryl chloride the fibres, fabrics, and films obtained from poly(vinyl alcohol).[108–110] It has been shown that an analogous reaction can also be achieved for other hydroxyl-containing polymers, for example, polyhydroxystyrene[111] and polydimethylethynylmethanol[112]. Phosphorus-containing poly(vinyl alcohol) has also been obtained by the reaction of poly(vinyl alcohol) with phosphoric acid in the presence of *N*-methylpyrrolidinone[113]. The phosphorylation of macromolecular compounds with phosphorus sulphide has been investigated in relation to polyethylene, polypropylene, polystyrene, polyacrylonitrile, and synthetic rubbers.

Polyethylene is phosphorylated in solution in chlorobenzene at temperatures in excess of 100 °C under a normal or excess pressure. The main reaction and subsequent hydrolysis of the PS_2 groups proceed via the mechanism[114]

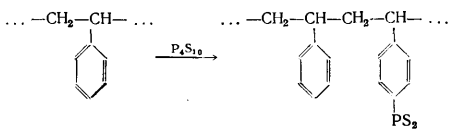


Depending on the reaction conditions and the reactant ratio, the phosphorus content in the product can vary from 3 to 10%.

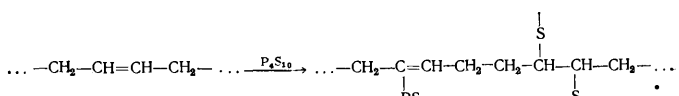
Polypropylene has been phosphorylated at normal and enhanced pressures and temperatures from 132° to 200 °C in an autoclave. The phosphorus content in the product did not exceed 1%. The low reactivity of polypropylene has been explained by the shielding of the tertiary carbon atoms by methylene groups[114]. The phosphorylated polypropylene contains up to 1% of sulphur, which corresponds to one sulphur atom for 75 elementary units of the polymer.

In the phosphorylation of polyacrylonitrile with phosphorus sulphide, it was possible to introduce only 0.5% of phosphorus into the polymer. As for polypropylene, despite the enhanced reactivity of the tertiary carbon atom, access to the latter is sterically hindered. Phosphorylation under more severe conditions makes it possible to increase the phosphorus content to 7.3%. When an attempt was made to hydrolyse the PS_2 groups in the phosphorylated polyacrylonitrile, the hydrolysis of the nitrile groups to carboxy-groups was noted at the same time.

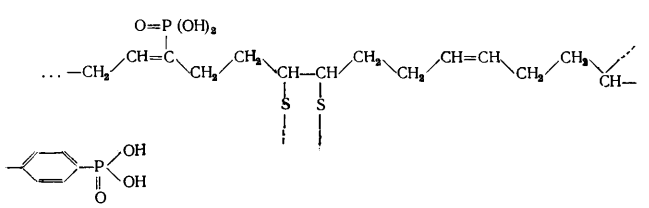
A study has also been made of the phosphorylation of polystyrene. This resulted in products in which a phosphorus atom is present in each second, fourth, or tenth elementary unit of the polymer depending on the conditions. The PS_2 groups enter preferentially into the *para*-position in the benzene ring[10]:



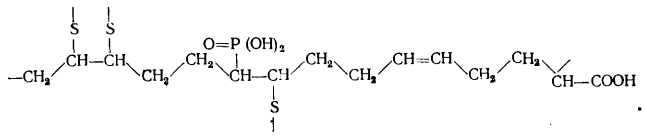
The phosphorylation of various raw rubbers has also been studied[115]. The phosphorylation of butadiene rubber proceeds via the mechanism



When the SKS-30 rubber was phosphorylated in solution in chlorobenzene at 132 °C, it was shown by infrared spectroscopy that the reaction involves both the carbon atoms of the main macromolecular chain and the phenyl substituent. The final product contains 11.5% of phosphorus and 22.7% of sulphur and has the structure



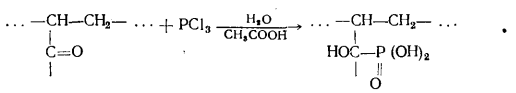
The phosphorylation of butadiene-nitrile rubbers proceeds with greater difficulty than that of butadiene–styrene rubbers. After hydrolysis, the products have the structure



All the phosphorus-containing polymers obtained are plastics insoluble in water, acids, alkali, and organic solvents. They melt at 200–300 °C and have ion-exchange properties.

A method of synthesis of polyphosphonothioic acid with a high molecular weight by the reaction of polyisobutylene with phosphorus pentasulphide in the presence of sulphur and followed by hydrolysis of the reaction product has been proposed[116]. Phosphorus-, sulphur-, and halogen-containing polymers, distinguished by an enhanced resistance to acids, have been synthesised by the reaction of polymers of aliphatic hydrocarbons (or their copolymers with vinyl acetate or vinyl chloride) with phosphorus trihalides and sulphur at temperatures exceeding 140 °C.[117]

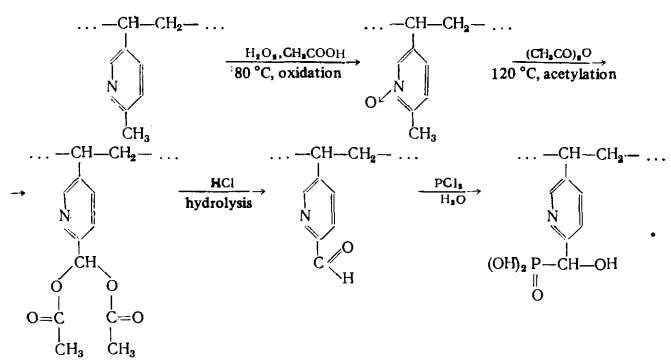
The reactions of carbonyl-containing polymers with phosphorus trichloride yielded polymers containing α-hydroxyphosphonic acid groups[118]:



The substrates can be both aliphatic polymers [for example, poly(methyl vinyl ketone)] and aromatic polymers (for example, acylated polystyrene).[119,120] The reaction also proceeds when an acylated styrene–divinylbenzene copolymer is used[121]. Treatment with phosphorus trichloride of a grafted *cis*-butadiene rubber–acrolein copolymer results in the formation of a structured product containing 0.5–0.7% of phosphorus and exhibiting an enhanced fire resistance[122]. The interaction of low-molecular-weight polybutadiene containing the OH and COOH groups with PCl_5 results in the phosphorylation of the polymer not only in the functional groups but also in the double bonds[123].

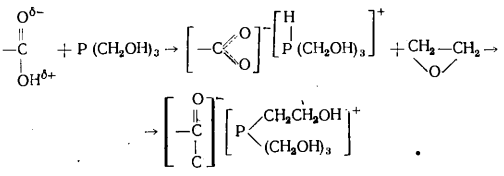
Phosphorus-containing polymers with ion-exchange properties have been obtained in the phosphorylation of polyacrolein[124] and acrolein-divinylbenzene copolymers by treatment with phosphorus trichloride[125].

Consecutive transformations of the copolymers of 2-methyl-5-divinylpyridine with divinylbenzene and di-isopropenylbenzene led to the synthesis of new phosphorus-containing pyridine polymers with ion-exchange properties[126]:

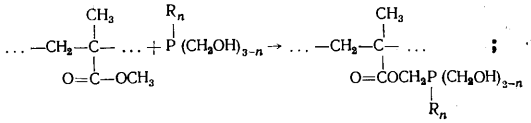


The products contain 8–9% of phosphorus and 5–6% of nitrogen and exhibit the maximum selectivity in relation to indium and uranyl ions.

The possibility of synthesising phosphorus-containing polymers by treating polyacrylic and polymethacrylic acid and also of copolymers containing carboxy-groups with tri(hydroxymethyl)phosphine (in the presence of epoxyethane) has been demonstrated[127]. The phosphorylation of polyacrylic and polymethacrylic acids was carried out using water as the solvent. The phosphorylation of carboxylate rubbers and methacrylic acid–styrene copolymers was performed in benzene or toluene. In the case of polymethacrylic acid in the presence of a threefold excess of phosphine, the degree of phosphorylation of the functional groups reaches 91%. For polyacrylic acid, the degree of phosphorylation is 59.8%. The properties of the products vary as a function of the amount of phosphorus introduced. Whereas the phosphorylated polyacrylic acid is a powdered product, polymethacrylic acid can be rubber-like after phosphorylation. The following reaction mechanism has been proposed:



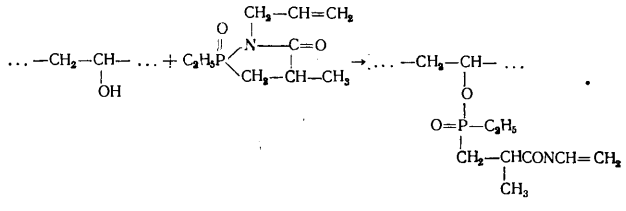
An attempt has been made to carry out the transesterification of poly(methyl methacrylate) by treating it with various phosphine derivatives[128]:



$R = CH_3$; C_3H_7; $C_6H_5CH_2$; $n = 0-2$

However, it was not possible to introduce phosphorus into the polymer, which the authors believe[128] can be explained by the influence of the substituent at the α-carbon atom, which hinders the transesterification.

Azophospholan has been used as the phosphorylating agent for polyhydroxy-compounds[129,130]. The interaction of azophospholan with poly(vinyl alcohol) proceeds analogously to its interaction with low-molecular-weight alcohols:

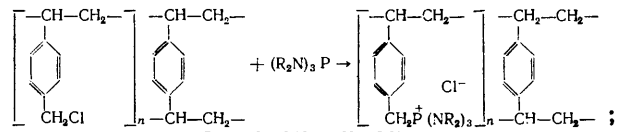


Up to 6.1% of phosphorus is introduced into the final product.

Phosphorus-containing derivatives of polyhydroxy-compounds have also been obtained using the anhydride of 4-hydroxy-4-oxo-4-phosphocaproic acid[131], 1-chloro-3-methyl-1-oxo-phosphocyclopentane[132], and acetyl phosphites[133] as phosphorylating agents.

Diethylphosphonoacetals of poly(vinyl alcohol) have been obtained by the reaction of diethylphosphonoacetaldehyde with partially acylated poly(vinyl alcohol).[134] The products synthesised are soluble in water and contain up to 8% of phosphorus.

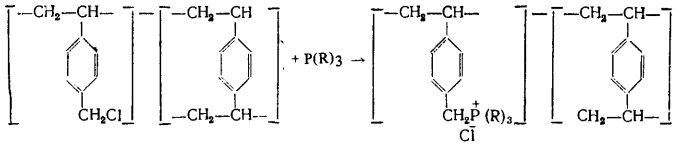
The reaction of the chloromethylated styrene–divinylbenzene copolymer with phosphorous acid amides yielded[135] the corresponding high-molecular-weight polymeric quasi-phosphonium salts:



$R = CH_3$; C_2H_5; C_3H_7; C_4H_9.

In order to increase the degree of phosphorylation, the reaction is carried out without a solvent in the presence of an excess of phosphorous acid amides in an argon atmosphere. The degree of phosphorylation is influenced not only by the reaction conditions but also by the structure of the groups in the amides, the degree of phosphorylation decreasing with increase of the bulk of such groups. It has been established that the maximum degree of phosphorylation is attained when the reaction is carried out at 120 °C for 10 h. The quasi-phosphonium salts are stable substances which do not change on refluxing ror 15 h in solution in aqueous dioxane in the presence of 0.1 *N* sodium hydroxide and in concentrated hydrochloride acid.

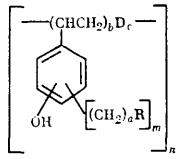
Phosphorus-containing polymers having the structure



$R = C_3H_7$; C_6H_5; CH_2OH

have been obtained by phosphorylating chloromethylated styrene–divinylbenzene or styrene–divinyl copolymers by various phosphines (in the presence of anhydrous aluminium trichloride as the catalyst or in its absence).[136,137]. Polymeric quaternary phosphonium salts containing more than 80% of phosphorus have been synthesised by the reaction of triethyl phosphite with chloromethylated styrene copolymers at 100–140 °C.[138]

Hydroxystyrene polymers, which incorporate phosphonium groups of the type



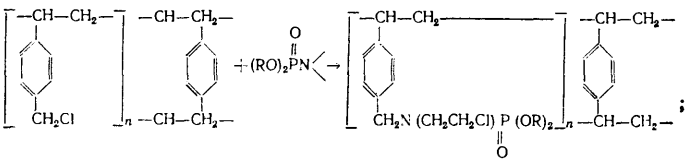
where $a = 0$ or 1, $m = 0-2$, $n > 3$, b is an integer, $c = 0$ or is an integer, D is a copolymer unit, $R = \overset{+}{P}(OR^1)_p \cdot (R^2)_{3-p}X^-$, $p = 1$, 2, or 3, $R^1 = C_{1-20}$ alkyl, $R^2 = H$ or C_{1-20} alkyl, and X = Cl, Br, or I, are formed when halogenated polyhydroxystyrene interacts with the triester $P(OR^1)_pR^2_{3-p}$.[139]

A method for the preparation, by an analogous reaction, of homogeneous ion-exchange membranes by phosphorylating with triphenylphosphine a chloromethylated polystyrene grafted to vinylidene fluoride–chlorotrifluoroethylene copolymer films has been described[140]. The membranes have a high exchange capacity and are incombustible.

According to Gorbunov et al.[141], phosphorus-containing polymers are formed when tri(hydroxymethyl)phosphines interact with the homopolymers and copolymers of unsaturated acid fluorides. The final products contain up to 12% of phosphorus and exhibit an enhanced fire resistance.

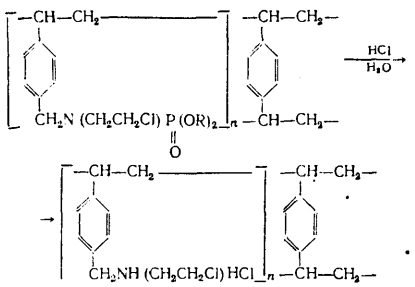
Water-soluble resins have been obtained as products of the reactions of a styrene–halogenomethylstyrene copolymer with a trisubstituted phosphine at 60 °C for 6 h.[142]

The interaction of the ethyleneamides of dialkylphosphoric acid with a chloromethylated styrene–divinylbenzene copolymer is accompanied by the cleavage of the ethyleneimine ring with formation of *N*-iminoethylation products[135]:

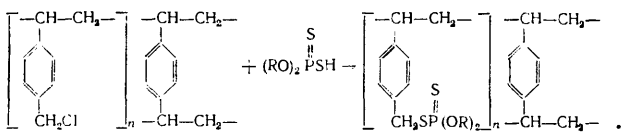


$R = CH_3;\ C_2H_5;\ C_3H_7$.

The *N*-phosphonaminoethylation products are unstable in an acid medium and are readily cleaved at the N–P bond with formation of dialkylphosphoric acid and the copolymer of the hydrochloride of (β-chloroethyl)vinylbenzylamine and divinylbenzene:

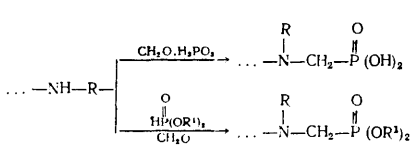


When a chloromethylated styrene–divinylbenzene copolymer is heated at 150 °C with *O,O*-dialkyl esters of phosphorodithioic acid in the absence of a hydrogen chloride acceptor or in its presence, copolymers of *O,O*-dialkyl *S*-(*p*-vinylbenzyl) esters of phosphorothioic acid and *p*-divinylbenzene are formed[143]:



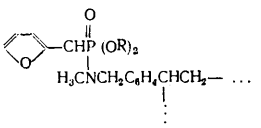
The degree of phosphorylation of the chloromethylated styrene–divinylbenzene copolymer depends on the size of the alkyl group in the *O,O*-dialkyl phosphorodithioic acid molecule and reaches 99.2%. With increase of the bulk of the hydrocarbon group, the degree of phosphorylation falls. The final product contains 3.9–9.6% of phosphorus and 8.7–19.7% of sulphur. The copolymers of *O,O*-dialkyl *S*-(*p*-vinylbenzyl) esters of phosphorothioic acid and *p*-divinylbenzene readily alkylate aliphatic and aromatic amines with formation of the salts of the corresponding tertiary amines and the copolymers of *O*-alkyl *S*-(*p*-vinylbenzyl) esters of phosphorothioic acids.

Primary and secondary amino-groups, introduced into the structure of the macroporous methacrylate–divinylbenzene copolymer by aminolysis with ethylenediamine and hexamethylenediamine condense with formaldehyde and phosphorous acid or its alkyl esters[144]:

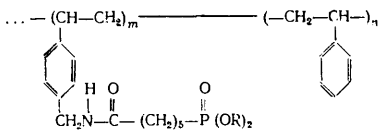


The phosphorylation of the aminated styrene–divinylbenzene copolymer proceeds via an analogous mechanism[145–147].

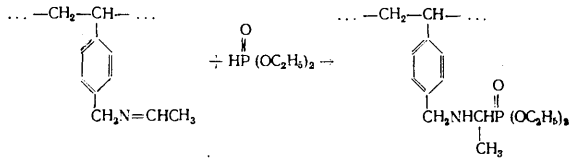
An anion-exchange resin, the elimination of the ester residue of which gives rise to an ampholyte with the *N*-methylamino-2-furylmethylphosphonic acid groups, has been synthesised by the amination of the chloromethylated polystyrene skeleton with the diethyl ester of *N*-methyl-α-amino-2-furylmethylphosphonic acid[148]:



A self-extinguishing polymer has been obtained by introducing a phosphorus-containing group into the *para*-position in the polystyrene molecule as a result of treatment of the polymer with 2-diethylphosphono-*N*-hydroxymethylacetamide, 2-dipropylphosphono-*N*-hydroxymethylacetamide, etc. in the presence of Friedel–Crafts catalysts[149]:



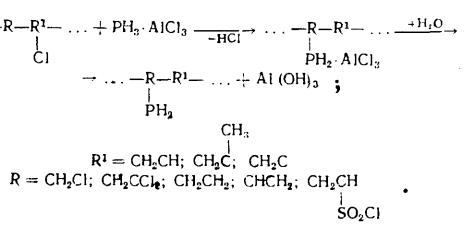
A polymeric complexone containing 8–9% of phosphorus and 5–7% of nitrogen has been synthesised by the condensation of dialkyl phosphites with the products of the interaction of aminomethylpolystyrene and acetaldehyde[150]:



Polymers containing phosphino-groups have been synthesised by the reaction of halogen-containing polymers [chloromethylated polystyrene, brominated polybutadiene, poly(vinyl chloride), and poly-*p*-bromostyrene] with metal phosphides in an inert solvent at temperatures from 40° to 200 °C.[151]

A self-extinguishing polystyrene containing the CH_2CH. $.[C_6H_4–CH_2P(O)(OR)_2]$ units, where R = alkyl or C_{1-8} cyclic alkyl, have been obtained by the interaction of alkali metal dialkyl phosphites with a partially chloromethylated polystyrene[152]. The reaction takes place at 40–90 °C for 6–8 h and the final product contains 5–10% of phosphorus.

The copolymer of chloromethylated polystyrene and divinylbenzene interacts with (β-diphenylphosphinoethyl)phenylphosphine treated with potassium in tetrahydrofuran, giving rise to three-dimensional products with diphosphine side groups[153]. Carbochain polymeric phosphines have been synthesised by phosphorylating halogen-containing carbochain polymers with a complex of phosphine and aluminium trichloride[154]:



The interaction is accompanied by a side reaction involving the elimination of hydrogen chloride and the consequent formation of polyene structures in the main macromolecular

chains. The degree of phosphorylation is greatly influenced by the temperature, the nature of the initial halogen-containing carbochain polymer and the Lewis acid. Depending on the reaction conditions, up to 18% of phosphorus is introduced into the treated polymers.

A mixture of red phosphorus and iodine can be used as the phosphorylating agent for chloromethylated styrene–divinylbenzene copolymers[155].

VII. APPLICATIONS OF PHOSPHORYLATED CARBOCHAIN POLYMERS

As mentioned above, phosphorylated carbochain polymers have found a wide variety of applications. Thus, phosphorylated styrene–divinylbenzene polymers containing phosphoric acid groups and exhibiting ion-exchange properties are widely used in the sorption of transition metal ions from solutions of alkali metal and ammonium orthophosphates, from chloride solutions with a complex salt composition, and from phosphoric acid[156–159]. Polyampholytes containing both nitrogen and phosphorus are capable of sorbing tellurium[160], beryllium[161], and nickel[162] ions from electrolyte solutions constituting the waste from the metal treatment industry and its waste water. Nitrogen- and phosphorus-containing amphoteric ion-exchange resins with aminomethylphosphonic acid groups can be used for the joint sorption of copper and zinc from sulphuric acid solutions[163], while polymers with hydroxyethylidenephosphinic acid have been recommended for the elimination of iron from phosphoric acid and electrolytes[164].

Ampholytes based on network copolymers of 2-methyl-5-vinylpyridine, combining in a single elementary unit of the network matrix both the pyridine and α-aminomethylphosphono-groups, are selective in relation to copper in the presence of cobalt, nickel, and iron[165]. Phosphorus-containing polymers with hydroxyaminoalkylphosphono- and ethylenediaminephosphono-groups sorb uranium from carbonate-containing solutions[166]. Carbochain polymers with difluoroalkyl phosphate groups in the side chain also exhibit complex-forming properties[167].

Phosphorylated copolymers of styrene with vinylphenols or the glycidyl ethers of vinyl phenols have been used as phosphorus-containing polymeric catalyst carriers, which are characterised by a pronounced ability to swell in hydrocarbon solvents and an enhanced stability[168]. Polymeric ligands for metal complex catalysts have been obtained by treating phosphorylated polymers containing aromatic rings with organometallic compounds[169]. Pyridinephosphineiridium complexes fixed on macroporous polystyrene–divinylbenzene polymers with phosphine groups have shown a high activity in the hydrogenation of olefins[170] and the hydridocarbonyltris(triphenylphosphine)rhodium complex on a styrene–divinylbenzene copolymer is an effective catalyst of the hydroformylation of propene[171].

Phosphorylated carbochain polymers have been used as stabilisers of the ageing of high-molecular-weight compounds. It has been shown for polyethylene that they are effective inhibitors of thermo-oxidative degradation[172] and can be used as anti-ageing agents for cured rubbers based on synthetic raw rubbers[173–175].

The products of the interaction of tri(hydroxymethyl)phosphine with carboxyl-containing chloroprene and nitrile elastomers have been used as adhesives for the attachment of various types of rubbers to metals[176], while cured rubbers based on phosphorylated carboxylate raw rubbers exhibit an enhanced resistance to benzene[177]. Phosphorus-containing ethylene–propene rubber increases the thermal stability and improves the working properties of lubricating oils[178]. The product of the interaction of low-molecular-weight polypiperylene with di-isopropylphosphorodithioic acid has been used as a polyfunctional additive to lubricating oils with effective antioxidant, antiwear, and antidrag properties[179]. Phosphorus-containing oligoisobutylene exhibits analogous properties[180].

The polyphosphonates obtained by phosphorylating polystyrene, poly(2,6-dimethyl-1,4-phenylene oxide), or the styrene–vinylidene chloride copolymer has been used to prepare semipermeable membranes capable of sorbing selectively individual organic liquids from their mixtures with other liquids[181].

The product of the interaction of the acrylic copolymer with phosphorus pentoxide has been used as a reactive organic phosphate catalyst for thermoreactive varnish coatings[182]. Phosphorus-containing polystyrene combined with carbon tetrachloride has been used in peptide synthesis[183]. Certain phosphorylated carbochain polymers exhibit bactericidal properties[184]. They have been used as polymerisation initiators[185], for the prevention of the formation of scale, and also as flocculants[186].

Thus the study of the phosphorylation of synthetic carbochain polymers is undoubtedly of both theoretical and applied importance and the search for new phosphorylating agents and the expansion of the assortment of polymers used in this process will create even greater possibilities for the practical utilisation of such products.

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Lignins as Components of Polymeric Composite Materials

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The results of studies of natural, native, and technical lignins are surveyed. Data are presented on the structures and physicochemical properties of various technical lignins (hydrolytic, sulphite, and sulphate lignins), which constitute the waste of the cellulose-paper and hydrolytic industries. Considerable attention is devoted to the examination of the properties of lignins which are responsible for their employment for the reinforcement of elastomers and the modification of plastics.
The methods of utilisation and rational employment of technical lignins in the plastics industry as active ingredients of polymeric composite materials are examined.
The importance of sulphate lignins as the most active from the standpoint of structure and properties in relation to the polymer matrix for the creation of highly filled lignin-containing polymeric materials—lignoplastics of the type of poprolin—is specially emphasised.
The bibliography includes 160 references.

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I. INTRODUCTION

The accelerated rate of growth of the industry of polymeric materials under the conditions of the world economic crisis, the exhaustion of the petroleum resources, and the deficiency of polymeric raw materials has faced science and industry with new tasks involving the extraction and effective employment of the existing reserves and also the rational utilisation of the available natural resources.

From this standpoint, one of the promising trends in the technology of the processing of polymers is the formation of polymeric blended and highly filled composite materials with high indices of physicomechanical and operational properties. For this reason fillers play a major role in the solution of this important problem[1].

Practical experience has shown that the introduction of low-molecular-weight and high-molecular-weight fillers of different chemical types into the polymer matrix makes it possible to alter specifically the physicomechanical, rheological, and thermophysical characteristics of the polymeric materials and the articles obtained from them[2].

The creation of highly filled polymeric composites containing more than 20% of the filler (by volume), which involves a decrease of the consumption of the scarce basic polymer and a reduction in the cost of the material, is exceptionally important. This requires in its turn the search for cheap mineral and organic fillers the raw materials for which are extensive and readily available.

Calcium carbonate, kaolin, talc, silicon dioxide, metal oxides, asbestos, wollastonite, etc. have come to be widely used as mineral fillers[3-5]. The waste from stone quarries and stone processing industries, namely finely fragmented tuff, is used for this purposes[7].

Among organic fillers, carbon black, cellulose, carbon and graphite fibres, sawdust, cotton, coke, starch, and certain other substances have found applications[5,8].

Lignin and their degradation products[9-11], as well as kerogens and their processing products[12,13], which constitute the waste of the sulphate-cellulose and shale industries, are extremely promising organic fillers.

In selecting the fillers for polymeric materials, preference is given to organic products active in relation to the basic polymer, which facilitates their "combination" and the conversion of the compositions into finished articles and improves their physicomechanical characteristics.

The most widely used organic fillers for polymers are various kinds of carbon black, which still remain of primary importance, particularly in the technical rubber industry, where they are used as agents reinforcing elastomers[9,14]. However, the group of thermoplastic materials, for which readily available fillers of organic origin must be sought, provides the greatest potential possibilities for the development of the manufacture of filled polymers.

Technical lignins, which were first used as reinforcing fillers in natural and cured rubbers[15,16] but which have hitherto found limited applications in the plastics industry, are of great theoretical and practical interest from this standpoint. Admittedly, in view of the deficiency of the primary polymeric raw material, interest in lignin as a filler for thermoplastics has greatly increased in recent years in connection with the possibility of its employment for the creation of composition materials based on thermoplastics and their industrial waste[10,11,17-21].

Lignins are natural organic raw materials, since they are constituents of wood and plants (their content in wood reaches 30%), where they play the role of lining agents[22], and are comparable in this sense to cement and iron concrete[23] (p.259). Thus lignins are one of the high-molecular-weight components of wood and occupy the second place (after cellulose) as regards their abundance throughout the world as organic polymeric substances of natural origin.

Lignins are not only lining materials but also reduce the permeability of cell walls and thereby play an important role in the transport of water, nutrient substances, and metabolic products. They also impart rigidity to the cell walls and, acting as an intercellular binder, impart to wood resistance to impact, compression, and bending. Lignification renders the woody tissue more resistant to the action of microorganisms.

The lignins present in plant tissues are referred to as natural lignins, protolignins, or lignins *in situ*. The term "native lignin" refers to the preparation isolated by Brauns's method[24].

When lignin is isolated from wood (delignification of wood), it undergoes significant chemical changes which depend on the method of isolation so that the lignins obtained under industrial conditions (technical lignins) are not identical in their structure to nature lignins.

Technical lignins constitute the waste of the cellulose-paper and hydrolytic industries and are utilised extremely irrationally—mainly by combustion[25,26]. However, the lack of reliable data concerning the structure of lignin precludes the determination of its behaviour in a polymer matrix and retards its employment as a filler of thermoplastics.

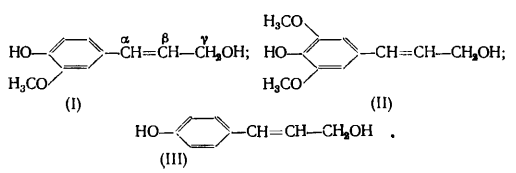
On the other hand, extensive theoretical and practical data have accumulated, which makes it possible to regard lignin as one of the promising fillers and modifying agents for polymeric composites (of the type of poprolin). It is therefore necessary to consider briefly the structure and properties of natural and technical lignins.

II. THE CHEMICAL STRUCTURE OF THE NATURAL LIGNIN MACROMOLCULE

The term "lignin" originates from the Latin word lignum (wood) and does not refer to an individual substance but to a group of related substances having common compositions, structures, and chemical properties for which Freudenberg suggested the term polylignols[27] and Shorygin suggested that they be referred to as lignin substances[28].

Lignin substances should be present in all plant tissues but some investigators hold the view that lignin appears in the course of the evolution of plants only in plants adopting a terrestrial mode of existence and that lignin is absent from seaweed[29].

At the present time lignins are understood as natural polymeric products formed by the enzymic dehydrogenation polymerisation of three main precursors: coniferyl alcohol (I), sinapyl alcohol (II), and *p*-coumaryl alcohol (III):[24]



The lignin macromolecule is formed in this process as a result of the combination of phenoxy-radicals, like other natural phenolic substances. Problems concerning the formation of the precursors of lignin and its biosynthesis in the plant cell walls *in vitro* and its chemical reactions have been described in detail in the literature[22,23,25-28,30-39] and there is therefore no necessity to dwell on them.

One should note that natural lignins undergo appreciable changes even on mild chemical treatment and for this reason methods permitting complete isolation of lignin from plants without the alteration of its chemical structure have not been found hitherto. The problem of obtaining ligning preparations analogous to natural lignin continues to be the most important in the chemistry of lignin.

Natural lignins have a number of specific properties: they are readily oxidised, they readily interact with chlorine, which is an important factor in the bleaching of cellulose, and they are soluble in alkalies on heating. This ability of lignin constitutes the basis of the alkaline delignification of the sulphate and soda methods of manufacture of cellulose, while its ability to dissolve on heating in aqueous solutions of sulphurous acid and its acid salts is used in the delignification of wood by the sulphite method[25].

Lignins are resistant to the hydrolytic action of solutions of inorganic acids and contain a large number of methoxy-groups, which serve as sources of methanol and unpleasantly smelling methyl-substituted sulphur compounds, and also several per cent of phenolic hydroxyls, which play an important role in the modification of thermoplastics[24,25,40].

The ability of lignins to be readily oxidised is used not only in the bleaching of cellulose but also in the preparation of a number of valuable products such as vanillin, vanillic acid, etc.[24,30]

Lignins from different plants differ appreciably in their structure and for this reason one distinguishes (1) conifer wood lignins, (2) deciduous wood lignins, and (3) grassy plant lignins. Conifer wood lignins have been most thoroughly investigated—they form a fairly homogeneous group of substances and even lignins from different conifer species have very similar properties. On the other hand, the lignins from deciduous tress and grassy plants have been less well studied and are distinguished by a wide variety owing to their complex chemical structure[22,24].

In the entire specialist literature on the chemistry of lignin, mention is made of the fact that its structure has been poorly investigated compared with a whole series of other substances with more complex chemical structures such as proteins, various enzymes, etc., which can be explained by the chemical inhomogeneity of the lignin macromolecule and the unsuitability of many classical methods of organic chemistry in the study of its structure. Therefore hitherto there is no formula which corresponds exactly to its real chemical structure.

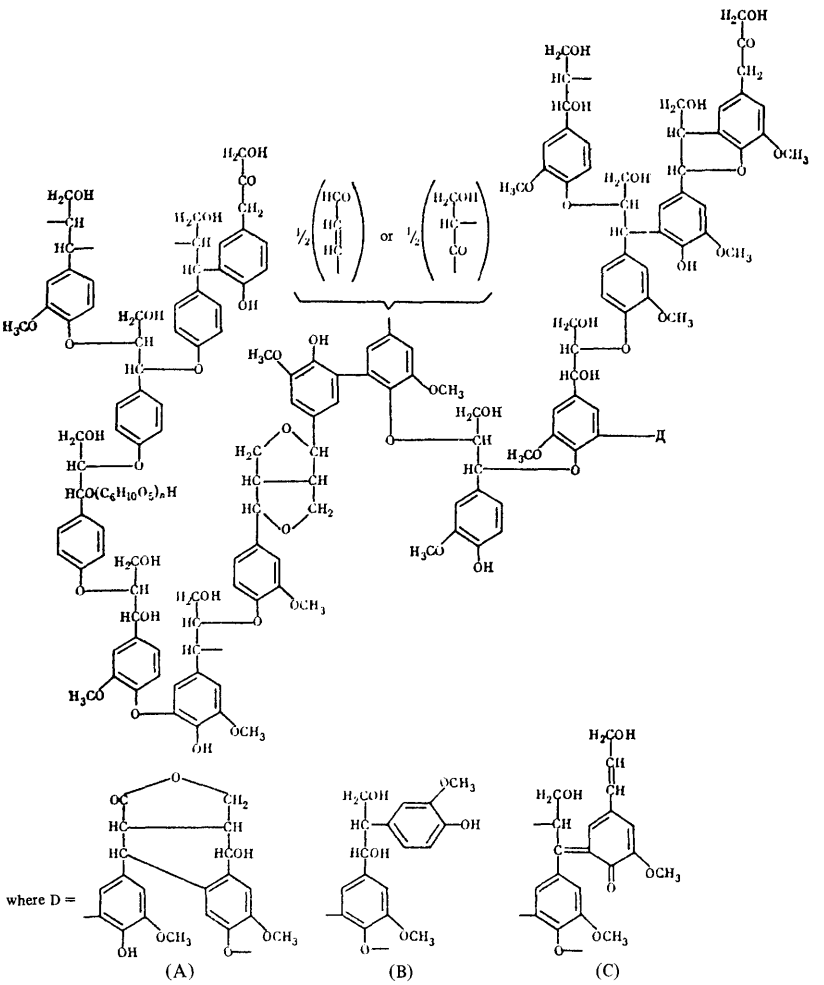
Among all the known hypothetical formulae, reflecting the chemical structure of lignin, that proposed by Freudenberg is believed to be the most successful. A fragment of the molecule of native lignin is presented in Scheme 1,[24] where D represents the possible versions of the dimeric unit (A, B, C).

Adler proposed an ionic mechanism for the biosynthesis of lignin, but here too the initial stage proceeds via a radical mechanism and without electron transfer[34,41], which is of significant interest for the explanation of the character of the interaction of lignin with thermoplastics when it is introduced into the polymer matrix.

Investigators who have studied lignosulphonic acids, which are formed in the bisulphite digestion of Norway spruce, reached an interesting conclusion concerning the structure of the monomeric unit of natural lignin. They subdivide the aromatic compounds of spruce wood into lignin and hemilignin (by analogy with cellulose and hemicellulose) and believe that certain contradictions in the chemistry of lignins are associated with the different contents of hemilignin in the lignin preparations investigated[42,43]. It was shown in these studies that spruce lignin has a high degree of structural homogeneity and is a polymer consisting of identical monomeric units, each of which contains 16 guaiacylpropane and two *p*-hydroxyphenylpropane groups, which corresponds to Freudenberg's structure of lignin and confirms yet again the agreement between Freudenberg's hypothetical formula and the real structure of lignin.

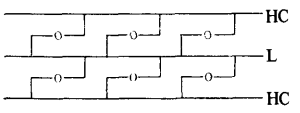
Data concerning the structure of lignin *in vitro* permit the next step—the elucidation of its "secondary" structure in plants (*in vivo*) taking into account the polymers surrounding lignin in wood, which have different compositions and structures[40,44].

Scheme 1



As pointed out by a number of investigators, lignin exists in plant tissue as a carbohydrate complex and is linked to the cellulose and hemicelluloses in wood, mainly via an oxygen bridge[30,45–47]. Lignin bound to hemicelluloses, namely hemilignin, must have a branched structure. The relative distribution of hemilignin (L) and hemicelluloses (HC) in wood is represented in Scheme 2 taking into account the lignocarbohydrate linkages[40].

Scheme 2



The molecular weight (MW) of natural lignins is comparatively high (of the order of several thousands, but is lower than that of technical lignins); they have a fairly porous structure and a large specific surface (the specific surface of native lignin is 180–280 $m^2 g^{-1}$).[22]

Thus natural lignin has a fairly high molecular weight and is located in wood between cellulose fibrils and is therefore accessible to the action of reagents only after the hydrolysis of the cellulose or the loosening of the fibrils with rupture of hydrogen bonds. The delignification of wood under industrial conditions and the preparation of technical lignins are based on this principle[22,25,26].

III. INDUSTRIAL METHODS FOR THE DELIGNIFICATION OF WOOD AND THE PROPERTIES OF TECHNICAL LIGNINS

The methods for the isolation of lignin from wood and other plant materials are based either on the dissolution of the carbohydrates present in wood and the preparation of lignin in the form of an insoluble precipitate (in the preparation of hydrolytic lignin) or on the dissolution of lignin with its subsequent precipitation (in the preparation of alkaline lignins and lignosulphonates)[22,25,48].

Three methods of processing wood are used in the USSR and the side products of these industries are various technical lignins.

1. By a hydrolytic procedure, in which wood is treated with a dilute solution of sulphuric acid, hydrolytic lignin being obtained in the form of a non-hydrolysable residue[25].

2. By the sulphite method, in which wood is treated with a solution of calcium, magnesium, or ammonium bisulphite and

sulphurous acid, sulphite lignin or lignosulphonates being obtained[25].

3. By the sulphate method, in which wood is treated with a solution of caustic soda and sodium sulphide with formation of alkali lignins (sulphate alkali or soda alkali methods depending on which reagent is used to make good the loss of alkali)[48].

In conjunction with modern technology, the sulphate method is the most economical (compared with the soda method) since the chemical reagents are regenerated in a closed system with a high technical efficiency, which makes it possible to eliminate completely the pollution of soil and water reservoirs. These advantages of the sulphate method of the manufacture of cellulose explain its vigorous development both in the USSR and abroad, where sulphate lignin is known mainly as Kraft lignin[22,48].

Sulphate lignins have the highest chemical reactivity compared with other technical lignins.

The structure and properties of technical lignins depend on the type of tree from which the wood has been obtained and the method of its treatment, i.e. are determined by the type of digestion process.

Like native lignins, technical lignins are polyfunctional high-molecular-weight aromatic compounds made up of phenylpropane structural units whose characteristic feature is an irregularity of structure and a wide variety of linkages; their density is in the range 1330–1450 kg m^3 and they have high specific surfaces (from several units to several hundreds of $m^2\ g^{-1}$ depending on the moisture content of the product) and a high refractive index (1.61) as a consequence of their aromatic nature[32]. The difference between the structures of technical and natural lignins are indicated by the results obtained in their investigation and the invstigation of model lignin compounds by physical methods[45,49–60]. The EPR method, which helps to elucidate the mechanism of the modifying action of lignin on thermoplastics in the formation of polymeric composites such as poprolin and lignoplastics, has acquired considerable importance in recent times[61–67].

The first studies designed to detect free radicals (R) in lignin by EPR date back to 1960.[52] The absence of a signal from specimens in the form of fresh dry undamaged wood filings from several trees was reported and the concept of the absence of R in natural lignins was adopted. As a result of the employment of a more sensitive EPR spectrometer, such signals were later detected in undamaged wood of black spruce[53]. It was then observed that the intensity of the EPR signal increases in pulped wood after mechanical treatment and that the intensity of the signal in technical lignins depends on the delignification conditions[53–56].

The results led to the hypothesis that the radicals R are formed as a consequence of the comminution of the rigid lignin network due to the mechanical or thermal degradation in the course of digestion at 180–190 °C and that R should be present in all technical lignins. In all the lignins investigated (regardless of the method of delignification) the EPR signals did not exhibit an appreciable hyperfine splitting. It was found that the lignins from deciduous and conifer wood contain approximately 10^{18} spins per gramme with g-factors of approximately 2.00.[24] The factor $g = 2.00$ confirms that the source of signals in lignins are the radicals R formed on degradation of the lignins and consist of molecular fragments with radical centres having a specific structure[56]. The nature of these paramagnetic centres has not been established but it is believed that they are radicals of the semiquinonoid type. Stable phenoxy-radicals have also been detected, which can be attributed to the dehydrogenation of lignins[57].

Questions involving the study of the free-radical processes in the delignification of wood are important both for a more accurate determination of the structure of lignin and for the explanation of the mechanism of its action when it is introduced into a polymer matrix as an active ingredient of the polymer composition.

These reactions have been studied in greatest detail for sulphate alkali lignin; the results of these studies are examined in the next section.

The thermal properties of technical lignins are significant for their employment in the preparation of polymeric composites because the latter are processed at temperatures in excess of 200 °C. Unfortunately, the existing fairly extensive information in the literature[24,68–73] does not provide an unambiguous answer to the question of the thermal stability of lignins in general and technical lignins in particular, which can evidently be accounted for by objective difficulties which hinder the determination of their exact chemical structure.

The available data on the thermal degradation of lignins indicate their different thermal stabilities, which are determined both by the kind of tree from which the wood has been obtained and by the delignification method[68,69]. It has been established that the lignin obtained from spruce wood has a higher thermal stability, regardless of the method of its isolation, than deciduous lignin; this is caused by the enhanced capacity for condensation processes in coniferous lignin as a result of the accumulation of C–C bonds at high temperatures. There are data showing that lignins are pyrolysed by a free-radical mechanism[105].

It has been shown that the methoxy-groups have the highest thermal stability in the lignin molecule, being retained on heating above 350 °C, and it is therefore to be expected that methoxylation is one of the effective methods for the retardation of the rupture of the alkyl–aryl ether linkages, whose thermal stability is lowest.

Methylation of lignins inhibits the dissociation of the alkyl–aryl ether linkage and not only does not increase but actually somewhat diminishes the overall thermal stability of lignin. The reason for this is that the stabilising effect of the methoxy-group introduced is swamped by the reduction of the number of C–C bonds as a consequence of the cessation under these conditions of the primary condensation process and the decrease of the capacity of lignin for secondary condensation[69], since two competing processes take place in it during heat treatment (at temperatures of 150–300 °C): primary condensation with participation of the hydroxy-groups of the propane chain and the formation of the C–C bonds between the structural units of lignin and the disruption of the weakest alkyl–aryl ether linkages.

Thermographic studies of technical lignins have shown that their thermal stability is not as high as has come to be believed. The temperature range of the softening (glass formation) of lignins varies within wide limits (from 120° to 250 °C) and depends on the method of isolation, the molecular weight, and the moisture content. For example, the glass point of dry native lignin is T_g = 130 °C and that of moist lignin is 50 °C.[24,30]

The structural changes in sulphate lignins due to the softening and compaction of macromolecules are observed already at 150 °C and above and the temperature range 240–360 °C is the region of active thermal decomposition, which takes place with a sharp increase in the number of paramagnetic centres via a free-radical mechanism[74].

It has been noted that the thermolysis of lignins takes place in two stages. The first stage, which occurs at comparatively low temperatures (100–250 °C), involves dehydration; the second high-temperature stage (250–350 °C) proceeds via a radical mechanism[71,74]. Under these conditions, even in a high vacuum and at a low rate of heating the weight loss in the first stage is more than 40% and that in the second is 12%.

IV. HYDROLYTIC LIGNIN AND ITS UTILISATION

Hydrolytic lignin (HL) is a waste product of the hydrolytic industry, which exists only in the USSR, and also of the processing of agricultural waste. When the entire capacity of the hydrolytic industry is utilised, more than one million tons of HL will accumulate annually in the waste. The solution of the problem of the utilisation of such waste is therefore urgently required.

Wood and agricultural plant waste are hydrolysed in special apparatus by percolating a hot 0.5–1% solution of sulphuric acid through a layer of hydrolysable material at 180–185 °C and pressures up to 144 mN m^{-2}.

Hydrolytic lignin is a polydisperse product with a particle size up to 1 cm and is a blend of substances of different chemical types. It incorporates comminuted polymerised lignin proper, polysaccharide residues, monosaccharides which were not washed off in hydrolysis, inorganic and organic acids, resins, waxes, nitrogen-containing substances, and ash elements[25]. In addition, it contains traces of furfural or hydroxymethylfurfural and its structure is that of a cross-linked polymeric product whose molecular weight as well as its chemical structure have not been accurately determined; HL is insoluble in organic solvents, alkalies, and acids.

Hydroltyic lignin is a hygroscopic product, so the moist lignin must be regarded as a three-phase system consisting of solid HL proper, water, and air[25,26,75].

Technical HL obtained in factories is usually highly contaminated by various impurities and its chemical structure varies, which greatly hinders its processing and utilisation both as a reinforcing agent and filler for plastics and elastomers[25,26].

Since HL has a cross-linked structure, it must be improved and modified before being introduced into polymeric materials. The modification of hydrolytic lignin consists in its treatment with active chemical reagents followed by nitration, sulphonation, phosphorylation, chlorination, and certain other reactions. Chlorination is regarded as one of the promising methods for its modification[76].

A number of realistic methods for the activation of HL involves the treatment with alkalies of its aqueous solutions at elevated temperatures (180–200 °C).[26] The mechanism of this process is not yet sufficiently clear, but there exists the view that the dissolution of lignin on treatment with an aqueous solution of alkali takes place as a result of the rupture of ether linkages with loss of methoxy-groups and the formation of free phenolic hydroxy-groups. At the same time the side chains are partly oxidised to carboxy-groups. Alkaline HL is a reactive product and can be used successfully for the reinforcement of elastomers together with sulphate alkali lignin.

Since, as stated above, HL is extremely hygroscopic, its internal surface area is determined by the moisture content (it is 760–790 $m^2\ g^{-1}$ for moist lignin and only 6 $m^2\ g^{-1}$ for dry lignin). The moisture content also determines the specific gravity and bulk density of lignin, which amount to 1500 and 200 kg m^{-3} for the dry product, the specific gravity of the product with 15% moisture content is 1300 kg m^{-3}, and the specific gravity and bulk density of the products with a 65% moisture content are 1150 and 700 kg m^{-3} respectively[77]. The angle of the slope of repose for crude lignin is 40–43°.

Hydrolytic lignin has a porous structure (the pore radius reaches from 30 to 200 Å) and has a low bulk density in the dry state, which reaches 190–220 kg cm^{-3}.

Since HL contains an increased amount of moisture as a consequence of its hygroscopicity and is a coarsely disperse system with a particle size up to 1 cm, before its utilisation it must be subjected to an additional treatment to increase the degree of its dispersion, which is achieved by additional drying, vibromilling, etc. The structural-mechanical (rheological) properties of HL and its capacity to absorb moisture are important for a theoretical justification of the rational drying regimes.

The study of the rheological properties of HL subjected to different degrees of processing and with different moisture contents showed that the general postulates of the physicochemical mechanics of disperse structures can be applied to it[75].

The methods for the utilisation of HL available at present cannot be regarded as rational and scientifically well founded. One of the simplest procedures for its utilisation involves combustion, since the industrial product is highly contaminated by non-lignin impurities and has a cross-linked structure, which creates additional difficulties in its employment. However, moist HL has a low heat generating capacity, which is 5500–6500 cal kg^{-1} for absolutely dry lignin, 4400–4800 cal kg^{-1} for the product with an 18–25% moisture content, and 1500–1650 cal kg^{-1} for lignin with a 65% moisture content, so that its employment as a fuel is ineffective. The low caloric value of HL as a fuel can be explained by the fact that lignin ejected from the hydrolytic apparatus has a moisture content in excess of 90%, so that for each tonne of lignin it is necessary to remove 900 kg of water and this requires a large amount of heat. The drying of lignin is also complicated by the fact that, like cellulose, it can form hydrates with water–lignin-OH.[77]

There exist also other methods for the utilisation of hydrolytic lignin although not on an industrial scale. For example, HL can be used to prepare high-quality brands of activated charcoal. There exist technological schemes which make it possible to obtain charcoal and also other products of the dry distillation of HL. The charcoal obtained is used to manufacture carbon disulphide and carbon tetrachloride, for the preparation of activated charcoal, and also in the manufacture of polymeric materials[25,26,78,79].

More promising ways of using HL involve its chemical reactions.

The oxidative hydrolytic cleavage of HL in an alkaline medium leads to the formation of a mixture of organic acids, which can be used in the yeast industry in the accumulation of the protein and yeast mass, which makes it possible to increase the yeast resources by 20%.[80,81]

The HL nitration products can be used in the drilling for petroleum and gas as substances which reduce the viscosity of clay solutions and the products of nitration with more concentrated (30%) acid can be employed as growth substances[79].

The most promising products are chlorinated hydrolytic lignins which have found applications as substitutes for natural tanning agents and as reinforcing agents for natural rubbers and their activities are similar to those of sulphate lignins[82].

The hydrogenolysis of HL yields between 60 and 85% of low-molecular-weight ether-soluble products which include up to 70% of phenols, most of which are capable of condensing with formaldehyde to form resins of the phenol-formaldehyde type (Novolak and Reson resins)[26,83]. Thus HL can serve as a source of aromatic phenolic substances and cheap biologically active compounds with a quinonoid structure.

In the course of the oxidative degradation of hydrolytic lignins, which is carried out in solution in ammonia at high temperatures (above 300 °C) in the presence of oxygen, the formation of low-molecular-weight acids is accompanied by the simultaneous oxidative ammonolysis reaction; it has been noted that it proceeds via a multiplicity of pathways owing

to the presence in the lignin macromolecule of a large number of functional groups having both the electron-accepting properties of the conjugation system and the electron-donating properties of the protons in the aromatic rings. The product of the oxidative ammonlysis of HL is ammonised lignin, which is characterised by a high content of strongly bound nitrogen not hydrolysable by acids, whose pyrolysis at temperatures up to 500 °C does not entail the formation of tars[84].

In oxidative ammonolysis, conjugated bonds accumulate in the lignin and, as a result of the incorporation of nitrogen in its macromolecule, its electrical conductivity rises sharply and its EPR signal intensifies, which indicates an appreciable delocalisation of the π electrons of the double bonds both within and between individual parts of the lignin macromolecule. As a consequence of the presence in HL of a system with conjugated bonds, it has the properties of an organic semiconductor, exhibiting paramagnetism, and its electrical conductivity is low[60,84,85].

One of the interesting features of the ammonised lignin as a product with the properties of an organic semiconductor is its catalytic activity in the decomposition of hydrogen peroxide. A distinct correlation has been noted between the catalytic activity of polymeric semiconductors having a conjugation system and their paramagnetic properties[84].

Ammonised lignin is biologically active. When it is introduced into soil in small amounts, the vegetative growth of the plant mass is found to be accelerated and the resistance to the action of decay-causing bacteria is enhanced.

Other applications of activated HL are also known, for example, in the preparation of its derivatives which are used as flotation agents instead of cyanides[86].

Hydrolytic lignin has also found applications in the manufacture of thermoplastics and reactoplastics[25,26,87-89].

A technology for the preparation of press-powders with heat and moisture resistances and improved dielectric parameters (compared with the press-powder from traditional resins of the 03-010-02 type), which can be used in the manufacture of electrotechnical articles instead of traditional resins, has been developed on the basis of the waste from the hydrolytic industry and agriculture[87].

Yet another promising application of HL in the plastics industry is the preparation from it of press-compositions for the manufacture of pressed articles at an elevated temperature with effective physicochemical parameters and reduced capacity for the absorption of water and susceptibility to wear. The optimum content of lignin is 10–15 wt.%, the sump and neutraliser sludge from the hydrolytic industry being used as a modifying agent, which greatly extends the material base for the manufacture of such articles and reduces their cost[89].

Since, in contrast to cellulose, stable colours can be imparted to HL by basic vat dyes, it has been suggested that lignin be dyed in order to modify its surface[25,88].

When insoluble dyes (Aniline Black, azo-dyes, etc.) are deposited on HL, its adsorption properties change significantly, so that the dyeing of lignin by appropriately selected dyes can be used in order to modify its surface properties. The dyed HL is of interest as an active filler for the poly(vinyl chloride) resin for the preparation of linoleum. The manufacture of such linoleum is very economical, because it makes it possible to reduce the consumption of the resin by 20–30% and the specific consumption of the plasticiser per m^2 of linoleum is reduced by 15–20%.[25] The dyed lignin can be employed as an active filler for thermoplastics, reactoplastics, and synthetic rubbers[88].

The considerable saving of thermoreactive resin is achieved by employing phenol-lignins or lignophenol-formaldehyde resins, obtained by the condensation of phenol and HL. Phenol-lignins are suitable for the manufacture of press-powders and their physicomechanical parameters are not inferior to those of the phenol-formaldehyde resin manufactured industrially[25].

One of the promising methods for the utilisation of lignin waste from the hydrolytic industry is its employment as thermally insulating materials; new methods of manufacture of constructional elements on their basis are being developed.

HL is used in the building industry, in the cement and brick industries (the preparation of lignoconcretes and other constructional materials based on lime, cement, and gypsum with added polymeric materials), in agriculture, and in other branches of the national economy[25,26,90], but the applications of lignin for these purposes are merely incidental and are not widely used on an industrial scale. Great potential possibilities for such employment of HL are inherent in the plastics industry, where the creation of filled polymeric materials using cheap active fillers constitutes an urgent problem[1].

V. SULPHITE LIGNIN (LIGNOSULPHONATES) AND ITS UTILISATION

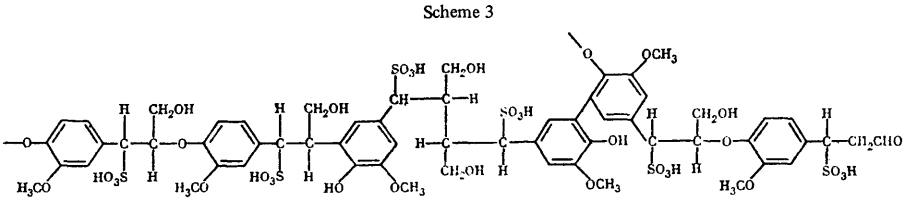
Lignosulphonates constitute the waste from the cellulose-paper industry in the manufacture of cellulose by the sulphite method. In this manufacturing cellulose-producing process, wood is heated with the digesting acid (an aqueous solution containing 2–10% of SO_2 in the form of free sulphurous acid and 1.3–2.5% of SO_2 as calcium bisulphite) with a stepwise increase of temperature to 145 °C. During the digestion, lignin is sulphonated. Almost the entire lignin and a large proportion of the carbohydrates accompanying cellulose can then be dissolved[25].

The chemistry of the sulphonation of lignin in sulphite digestions has still not been unambiguously elucidated but it has been shown that it may entail not only the sulphonation of lignin with formation of SO_3H groups but also the introduction of sulphate groups with formation of acid sulphate esters $R-OSO_3H$, in which the bond between sulphur and lignin is formed via oxygen[91].

The spent sulphite liquors contain aromatic substances whose composition is similar to that of lignosulphonic acids.

The lignosulphonic acids obtained in the manufacture of sulphite cellulose in the form of salts (calcium, sodium, ammonium, or magnesium lignosulphonates) have a variable composition, particularly as regards the content of carbonyl groups,

Scheme 3



depending on the degree of sulphonation and the methods of isolation. They are soluble in water, are titrated like strong inorganic acids, and are polyelectrolytes[92].

These acids constitute a polydisperse system with a wide range of molecular weights (2000–100 000).[30] The molecular structure of such an acid consists of a disordered, entangled, branched helix. The chemical structure of lignosulphonates has not been established, but by convention it can be represented in terms of the formula in Scheme 3.[25] During sulphite digestion, a major proportion of the lignin, in the form of lignosulphonic acids containing 4–6% of sulphur which form acid-containing groups of different strengths in the lignin[93], a large proportion of hemicelluloses, and other polysaccharides (including a certain amount of cellulose), tannins, and many inorganic subbstances pass into solution in the sulphite liquor[94].

The waste from the sulphite-cellulose industry consists mainly of the calcium salts of lignosulphonic acids and sugars [polysaccharides (pentoses) and monosaccharides (hexoses)] in proportions of approximately 2 : 1.[25] The reactions occurring in sulphite digestions have been examined in detail in the literature[23–25]. Valuable information about the structure of sulphite lignin is quoted by Forss and Fremer[42].

The hydrolytic and sulphonation reactions occurring in the acid treatment convert lignin into lignosulphonic acids with an extremely wide variety of molecular structures, including high-molecular-weight products with molecular weights in excess of 40 000. The content of such high-molecular-weight products is insignificant.

In order to isolate the lignosulphonates, the sulphite liquors are subjected to biochemical processing after separating cellulose, which results in the formation of a concentrate used for technical purposes.

Lignosulphonates are also manufactured in the form of liquid products and their amount manufactured in this form is ten times greater than in the solid state[94].

Free radicals, probably formed in the depolymerisation of lignosulphonates which constitutes a set of free-radical processes, have been detected in the lignosulphonic acids obtained from sulphite digestions[42,46,56]. However, the nature of these radicals could not be identified.

Thus the sulphite lignin in the form of lignosulphonates is the lowest-molecular-weight product among all the technical lignins and is characterised by a high solubility, also in water, and its principal practical applications are associated with this factor.

The varied applications of lignosulphonates substituted by univalent, bivalent, or polyvalent metals in various branches of industry and agriculture are based on their use as ion-exchange compounds, dispersants, surfactants, and fillers for natural tannides; their adhesive properties are also employed[25,26,94].

Lignosulphonic acids are of great interest as raw materials for the preparation of vanillin and vanillic acids[94].

Other applications of lignosulphonates are also known and these can be expanded by developing an extremely interesting method of biochemical processing of the organic materials in the liquor using not only carbohydrates but also lignin substances[86].

VI. SULPHATE ALKALI LIGNIN (KRAFT LIGNIN) AND ITS APPLICATIONS IN THE MODIFICATION OF POLYMERIC MATERIALS

Among all the types of industrial lignins, sulphate lignin, whose manufacture reaches an appreciable volume in view of the fact that three-quarters of the world production of cellulose (approximately 10 million tonnes annually) involves the sulphate method (the Kraft process), is most widely used in all industrial countries possessing wood as a raw material.

Alkali lignin is obtained as industrial waste in the manufacture of Kraft cellulose, where a mixture of sodium hydroxide and sodium sulphides is used as the base. The soda and sodium sulphate methods of preparation of cellulose are available. In these procedures wood is treated with a solution of alkali at 165°–175 °C.[48]

The principal difference between the soda and sodium sulphate methods of preparation of cellulose consists in the fact that the losses of part of the alkali, inevitable in the manufacturing process, are made good in the first instance by the addition of soda and in the second by the addition of sodium sulphate. The soda lignins are less soluble in organic solvents and are apparently more condensed than the sulphate lignins[95].

The spent dark solution obtained as a result of the digestion is called the black liquor and contains, together with inorganic substances, approximately half of the organic components of the initial wood, most of which is lignin. Since the technological cellulose digestion process by the sulphate method does not differ significantly from the soda method and the economic gain is fairly considerable, the sulphate method has almost completely displaced the soda method at the present time and henceforth we shall be dealing with sulphate alkali lignin or Kraft lignin.

The sulphate alkali lignin is sometimes called (not entirely correctly) "thiolignin", since a certain amount of organically bound sulphur (up to 2.5–3%) has been detected in it. However, this question remains controversial. It is most likely that the sulphur bound in organic compounds at the beginning of the sulphite digestion is split off during the subsequent digestion process and that the residual sulphur in the final product—the sulphate lignin—is most likely to be merely part of a side product stabilised as a result of side reactions[23,95].

In the sulphate method of manufacture of cellulose, virtually the only method of utilising the lignin obtained in the form of the black liquor remains its combustion. The part of the lignin contained in the "weak" liquor resulting from the washing of the cellulose and in the waste from the decomposition of the sulphate soap enters the waste water and pollutes it (waste water lignin).

In the Soviet Union and abroad rational ways of utilising sulphate lignin are being sought. The solution of this problem is at present urgently required also because in the industrial manufacture of cellulose an enormous amount of black liquors and waste water accumulate and their main organic component is lignin. In contrast to the other technical lignins isolated, Kraft lignins contain an increased amount of active acid groups (phenolic and hydroxyl), which largely determines their reactivity and the possibility of their practical employment for the reinforcement of rubbers and in the plastics industry. Sulphate lignins are therefore the most reactive and exhibit the highest chemical stability.

The difficulties in the employment of sulphate lignin are associated with the necessity to isolate it from the black liquors with a high yield of the lignin itself and this requires the development of a special technology[96,97].

For economic reasons, only two neutralising agents can be used to isolate lignin from the black liquor: H_2SO_4 and CO_2. When CO_2 is used, the yield of lignin is from 30% (carbonation without the application of pressure) to 70% (carbonation under pressure) of the amount present in the black liquor, while in the case where sulphuric acid is used, the amount isolated is in excess of 90%. A technology for the isolation of the carbon

dioxide and sulphuric acid sulphate lignins has been developed in the USSR. The chemical reactivities of these lignins hardly differ. However, the intrinsic cost of the carbon dioxide lignin (135 roubles per tonne) is 1.5 times higher than that of the sulphuric acid lignin[98,99].

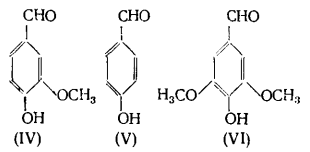
Pine, spruce, fir, larch, aspen, birch, popular and other types of wood as well as reeds, straw, and sawmill and wood processing waste are used as raw materials in the sulphate cellulose industry.

In the course of alkaline digestions and during the isolation of lignin from the black liquors, complex transformations associated with the rupture of hydrogen bonds under the influence of sulphide ions and alcoholic hydroxyls take place in the protolignin molecule, which greatly alters the structure of the Kraft lignin.

1. Characteristic Features of the Chemical Structure of Sulphate Lignin

Sarkanen, one of the senior foreign investigators of the chemistry of lignin, pointed out that the sulphate lignin precipitated from the black liquors on acidification is an ill-defined substance containing 2–4% of sulphur. However, its chemical structure is closest to that of natural lignin[72,100].

Bogomolov[48,96–98,101] and a number of foreign investigators[24†,55,102] have played a considerable role in the alkaline delignification of wood and the determination of the structure of sulphate lignin. The alkaline digestion of wood in the manufacture of cellulose constitutes a complex set of processes of different kinds, both chemical and physical. The chemical structure and properties of the resulting Kraft lignins are then significantly influenced by the conditions of the digestion and the origin of the wood employed (coniferous or deciduous)[24,25]. Lignins from gymnosperms (coniferous lignins) and lignins from angiosperms (deciduous lignins) differ in the products of their nitrobenzene oxidation: coniferous lignins give rise mainly to vanillin (IV) and small amounts of *p*-hydroxybenzaldehyde (V), while coniferous lignins produce vanillin and syringaldehyde (VI):



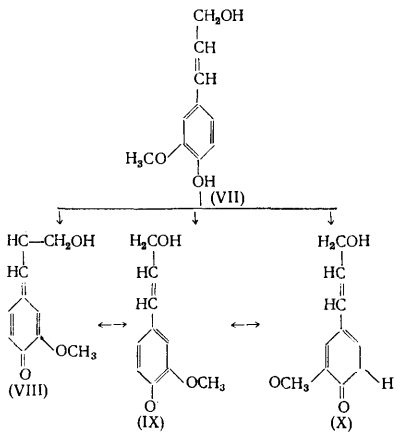
The chemical structure of the sulphate lignin isolated from the black liquors in the alkaline digestion has been examined and its various functional groups have been described in detail[24,102]. Reliable data have been obtained showing that the main bulk of the phenylcoumarin structures are converted during treatment into stilbene structures[30], which are formed when the radicals combine in accordance with Scheme 4 and apparently persist in the sulphate digestion and are present in Kraft lignin[28,30,102].

The stilbene structures cause the high reactivity of sulphate lignins and the reinforcement of polymers treated with such lignins.

† Chapter 12.

It has been established that Kraft lignin contains a considerable amount of phenolic hydroxyls, catechol groups, unsaturated quinonoid structures, aliphatic COOH groups, and other active structural elements containing double bonds.

Scheme 4



The principal distinctive feature of sulphate lignin is the presence of bound sulphur in amounts ranging from 1.5 to 3.0%, depending on the digestion conditions and the method of isolation of the lignin. A fragment of the structure of the sulphate lignin macromolecule is presented in Scheme 5:[28]

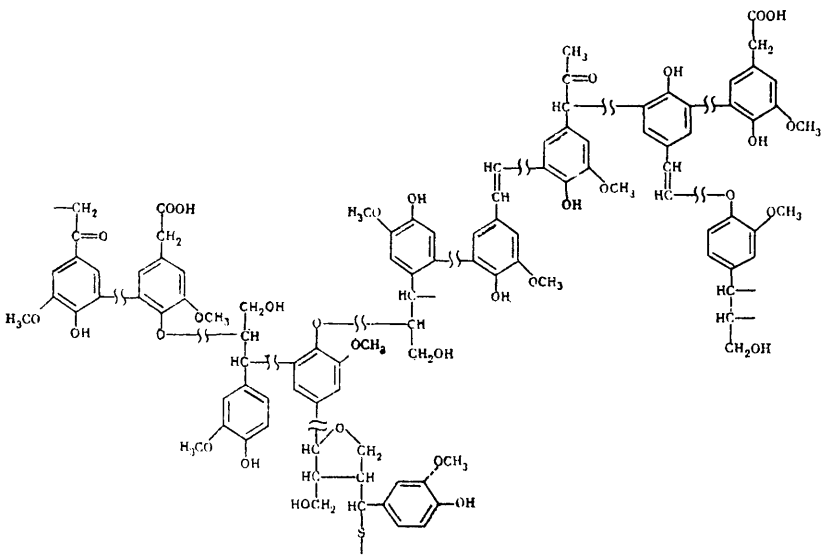
The alkaline digestion process constitutes a set of chemical reactions: the penetration of chemical reagents, the dissociation of lignin–carbohydrate linkages, thermal degradation of the lignin macromolecule, secondary reactions involving the condensation of fragments of this molecule, the removal of products from the reaction zone, etc. The reactions occurring in the alkaline digestion have been described in detail[24,30].

2. The Properties of Sulphate Lignin Responsible for Its Utilisation for the Reinforcement and Modification of Polymeric Materials

The EPR study of the paramagnetic properties of lignin provides great possibilities for the determination of the structures of native and technical lignins and also for the estimation of the modifying effect of Kraft lignin. As mentioned above, paramagnetic properties are characteristic of all kinds of technical lignins[42,56,60,85,94]. Free radicals were first detected in Kraft lignin by Kleinert and Marton[53] and these studies were continued in the cell of the EPR spectrometer in which wood was subjected to alkaline digestion[24,57,58]. It was established that the formation of the radicals R is the principal feature of the thermal wood delignification reactions and takes place when different methods are used for the delignification of wood at high temperatures (160° to 190 °C) regardless of the chemical nature of the raw material employed[24,54,56–58].

Free-radical reactions play a very important role in the alkaline delignification of wood particularly under the conditions of high speed digestions[54,55]. It has been noted that the concentration of the radicals R increases almost linearly with increase of the digestion time from 5 to 20 min (approximately in the first 0.5 h) and after the attainment of a

Scheme 5



maximum the concentration of R diminishes. This is probably a consequence of the fact that the alkaline delignification can involve two independent processes: degradation of the Kraft lignin macromolecules accompanied by an increase in the concentration of R and a decrease of the molecular weight and the subsequent condensation of the decomposition products accompanied by a decrease of the concentration of R and an increase of the molecular weight of the product.

However, when sulphate lignin is used for the modification of polymeric materials, it is necessary to know the character of the radicals R formed in it. Difficulties arise in the solution of this problem because it is impossible to resolve the hyperfine structure of the EPR spectra of the R formed. Many workers believe that natural lignins do not contain R at all and that the latter arise only on delignification of wood or in the course of its biological decomposition. The radicals R can also be formed as a result of the mechanodegradative processes during mechanical treatment with dissociation of covalent bonds[45,52,53,56,59].

This process has remained controversial hitherto, although recently it has been possible to obtain the EPR spectrum of Kraft lignin with a distinctive hyperfine structure at room temperature[45]. With increase of the digestion time, the spectrum changes: the signal loses its hyperfine structure and becomes of the singlet type. The EPR data for the soda and sodium sulphate treatments differ. Thus in the soda treatment the intensity of the EPR signal initially decreases and after a certain time (40 min) reaches a constant value, which permits the conclusion that two types of radicals are generated: unstable radicals whose concentration decreases with time from the start of the experiment and stable radicals whose concentration remains unchanged for 40 min.

In the sulphate treatment the hyperfine structure of the EPR spectrum was less distinct and disappeared faster than in the soda treatment. Furthermore, only a decrease of the EPR signal intensity was noted in the sulphate treatment.

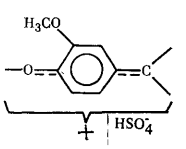
Comparison of data for the variation of the intensity of the EPR signal of lignin in the soda and sodium sulphate digestions shows that the influence of sulphur in the alkaline treatments can be explained by the inhibition of radical processes. When reducing agents (for example, sodium tetrahydroborate) are added to the liquors, the concentration of R falls and the hyperfine structure decreases much faster than in the soda digestion. The primary electronic excitation centre in the lignocarbohydrate complex is a semiquinonoid radical formed, which is fairly stable for some time[45].

The reactions of the radicals formed in the alkaline digestion cause the cross-linking of lignin and the increase of its molecular weight during the initial periods of the digestions. Inhibition may be achieved by introducing reducing agents ($NaBH_4$, Na_2S, cysteine, hydrazine, and thioglycolic acid). whose reduction potential is higher than that of lignin and carbohydrates in an alkaline medium, and by recombination reactions between lignin radicals and a specially introduced substance[103].

There exist two points of view concerning the nature of the increase of the molecular weight of lignin in alkaline digestions: the first explains the increase of the molecular weight by polycondensation processes and the second—by the interaction of the radicals. Both concepts remain controversial.

In addition to the view which explains the paramagnetic properties of lignin by the formation of the radicals R, it has been suggested that the paramagnetism of lignin has a radical nature[104] which for technical lignins is attributed to the presence of paramagnetic carbonium centres in their molecules.

Stable carbonium centres are formed in all technical lignins, and their stability can be explained both by steric factors and by their ability to combine with anions in solution to form carbonium salts:



The proposed mechanism of the formation of carbonium centres makes it possible to discover the cause of the differences between the sodium sulphate and soda digestions and also to explain the sharp increase of the EPR signal intensity of alkaline preparations of lignin in protic solvents, for example, in concentrated sulphuric acid. The stability of the paramagnetic carbonium ions may be influenced favourably also by other nucleophilic additives, such as amines, mercaptans, etc.

Taking into account the latter data, one may assume that the real nature of the paramagnetism of lignin is of a dual kind.

Interesting results have been obtained on irradiation of lignin and its model compounds with ultraviolet light at a wavelength of 300–400 nm directly in the EPR spectrometer[68]. The resulting spectra permitted the conclusion that phenoxy-radicals are formed preferentially.

The formation of phenolic compounds in the thermal decomposition of lignins, including alkali lignin, has also been discovered[70,73].

The inhibiting role of lignin (as a result of the formation of quinone methide structures) is indicated by the data of Zoldners et al.[105] The results reveal yet another promising application of lignin as an inhibitor and stabiliser with respect to the action of light for polymeric materials and compositions based on them (particularly compositions based on polypropylene), since there is a correlation between the stability of organic free radicals and the efficiency of their reaction[106].

Sulphate lignin is a lamellar amorphous polymer with a polydisperse structure which tends to undergo association and is characterised by a definite molecular order in its structure[107,108].

The molecular weights of Kraft lignins were first determined by Marton, Marton, and Lindberg[102,109,110] by different procedures and in different solvents and showed a fairly wide scatter: the weight-average molecular weight $\overline{M}_w$ was in the range 5600–25 000 and the number-average molecular weight $\overline{M}_n$ was in the range 1000–20 000. The ratio $\overline{M}_w/\overline{M}_n$ was 2.2 for the sulphate lignin from conifers (pine lignin) and 2.8 for the sulphate lignin from deciduous trees, which may indicate an appreciable dispersity.

The study of the molecular weight and the molecular weight distribution (MWD) of sulphate lignins showed that $\overline{M}_w$ of lignin is determined both by the digestion temperature and the sulphide content of the digestion liquor[96,111,112]. The values of $\overline{M}_w$ obtained for sulphate lignin varied from 4000 to 24 000 for digestions according to isotypical plots and from 7000 to 31 000 for stepwise digestions. The soda lignins isolated from the mass of cellulose in the soda digestion had a higher value of $\overline{M}_w$ than sulphate lignins.

The wide range of variation of the $\overline{M}_w$ of sulphate lignins cannot be attributed solely to the method of measurement of their molecular weight. It is probably caused by the different degrees of degradation of the soluble lignin in the digestion process or, possibly, by the association of the alkali lignin in solution, which was not taken into account in the early investigations[30].

Like lignosulphonates, sulphate lignins with a low molecular weight exhibit a high dispersing power, which is determined from the decrease of the viscosity of an aqueous suspension of rutile (titanium dioxide) on dissolution of a specific amount of lignin. The high dispersing power of Kraft lignin led to its employment in the form of industrial colloids (dispersants, binders, fillers, and gel-forming agents)[24] (Chapter 13).

A sulphate lignin paste for the building materials industry and powdered sulphate lignin for the technical rubber article industry are manufactured in the Soviet Union. The study of the properties of sulphate lignins produced by industry showed that they consist of products with a fairly high molecular weight of 4500–7500 and a degrees of polydispersity of 3.3–3.9.[97]

Technical lignin is a brown powder with a particle size from 100 to 200 μm, the 100–125 μm particles constituting the largest fraction. Particles of this size are largely spherical in a slightly fused envelope, while the larger particles consist of aggregates of the spherical particles. When sulphate lignin is dried (in the upper drying chamber) and also when it is vibromilled, not only its aggregates but also the spherical particles themselves are disrupted.

The vibromilled lignin particles have a high specific surface (up to 23 $m^2\ g^{-1}$) and are characterised by an excess of free energy, which may be the cause of their adhesion to one another and the formation of a complex of secondary particles whose size approaches to the optimum particle size of the non-comminuted lignin. The density of Kraft lignin is approximately 1300 $kg\ m^{-3}$.[22]

When the optimal technological parameters are maintained in the manufacture of sulphate lignin, the finished product has a fairly constant functional composition in terms of the ash, acid, and sulphur contents as well as the contents of water-soluble and tarry substances.

The infrared spectra of industrial batches of sulphate lignin are fairly isotypical both as regards the presence of absorption bands at the same wavelengths and the relative optical densities.

The thermal properties of lignin were already noted above. The presence of lignin in wood is the cause of its thermal softening, which begins in the temperature range 120° to 160 °C. The softening temperature (glass point) of lignin varies appreciably depending on its source and method of isolation[24] (Chapter 13). Sulphate lignins sinter at approximately 200 °C and tend to pass to a fluid state at elevated temperatures.

Important properties of sulphate lignin include its capacity for adhesion, which is a function of temperature, and its sorption properties[24,113].

On treatment with water, the degree of sorption of moisture increases, moisture acting as a low-molecular-weight diluent which reduces the transition temperature (T_g).

The solubility of lignin in various solvents depends on its sorption properties. It has been established that the action of solvents on lignin is a function of the cohesion energy density and the ability of the solvent to form hydrogen bonds. The maximum solvent power in terms of the Hildebrand parameter δ, defined as the square root of the cohesion energy density, is then observed for $\delta = 11\ cal^{1/2}\ cm^{-3/2}$. The solvent power of solvents with δ between 10 and 11 in relation to lignin increases with increasing ability of the solvent to form hydrogen bonds.

The study of solubility data has shown that the behaviour of lignin with respect to solvents and other macromolecules cannot be explained solely on the basis of the parameter characterising the ability to form hydrogen bonds, whose measure is the shift $\Delta\lambda$ of the infrared absorption of the OD group when the solvent is mixed with CH_3OD. However, water, which is usually a "poor" solvent for lignin, has the very high parameter $\delta = 23.4\ cal^{1/2}\ cm^{-3/2}$. On this basis one may conclude that, in estimating the solubility, one must take into account the overall effect of the polarity of the solvent molecules[110].

It has been shown that the fractions of lignin with a smaller molecular weight are soluble in solvents with a wider range of δ and $\Delta\lambda$ than the fractions with higher molecular weights. "Good" solvents for lignins must have $\delta \cong 11$ and $\Delta\lambda \geq 0.14$.[114]

From this standpoint, "good" solvents for sulphated lignin are dimethyl sulphoxide, dimethyl formamide, acetone, dioxane, pyridine, ethanol, methylcellosolve, and certain others, while "moderate" solvents are ethyl acetate and others[110].

Evidently the infrared spectra and solubility parameters of lignin provide information about its molecular size, the nature of its intermolecular interaction, and the general properties of the product. This applies particularly to the interaction with a single solvent. When mixed solvents are used, the problem is greatly complicated, but, with the aid of the two-parameter theory, it is possible to predict roughly the relation between the structure and solubility of lignins in binary and even ternary systems in terms of the reaction parameter (the Flory parameter).

3. Other Types of Sulphate Lignins

(a) *The ligno-tail product of the sulphate-cellulose industry.* In the alkaline delignification of wood, not only lignin but also resin and aliphatic acids, neutral substances, phenols, a proportion of carbohydrates, and other substances of organic and inorganic origin forming part of wood pass into the digestion solution called the "black liquor"[48]. When the black liquor is allowed to stand, the resin and aliphatic acids in the form of sodium salts coagulate and rise to the surface entraining the accompanying substances. The coagulation product is called the sulphate soap which has a complex composition, containing lignin and lignin-like substances among others.

The sulphate soap is in its turn decomposed with sulphuric acid, after which the reaction mixture is divided into three-layers: the tall oil brick, crust, and solid salts. The reaction mixture prior to separation into three layers is called the ligno-tall product and is a valuable raw material for the regulation of polymeric materials. The ligno-tall product (a mixture of tall oil and crust—lignin and lignin-like substances) contains up to 60% of tall oil, which is a mixture of aliphatic and resin acids, an insignificant amount of non-hydrolysable products, and approximately 40% of lignin.

The ligno-tall product (LT) can be obtained by mixing the markedly dustlike sulphate lignin powder with tall oil in proportions of 2 : 1.

The waste from the sulphate-cellulose industry can also be used to obtain the LT product: the acid water from the sulphate soap decomposition apparatus, light oil, pitch, etc.[97] A distinctive feature of the LT substances obtained in this way is a high ash content, which necessitates the removal of inorganic substances from them.

The LT substances can be mixed with a suspension of sulphate lignin in proportions of 1 : 2 and the new suspension of tall oil and lignin then yields a crude ligno-tall product which has approximately the same characteristics as dry powdered sulphate lignin. The applications of these lignins in the polymeric industry are approximately the same.

(b) *Lignin obtained from waste water (sludge lignin) from the sulphate-cellulose industry.* When the waste water from the sulphate-cellulose industry is purified, a large number of wash waste is produced—a sludge, which consists of waste water lignin and is a valuable chemical raw material. The sludge lignin provides a virtually inexhaustible source of raw material, since it accumulates in enormous amounts in waste dumps after the waste water has passed through the biological and chemical purification stages[99,115].

Industrial waste water from the sulphate-cellulose manufacturing process contain a large amount of lignin and organic substances. The purification of such water and the processes whereby they are rendered safe are achieved by a biological or chemical method and in many instances, when extensive purification is required, a combined method of purification is used.

The biochemical purification consists in the reduction of the biological and chemical consumption of oxygen as a result of the oxidative action of the "active silt" and the adjustment of the oxygen content to the norms established by sanitary requirements for industrial water released into water reservoirs. However, after such purification a considerable amount of dissolved organic substances remains in the water.

In the subsequent chemical purification of waste water by treatment with flocculants (aluminium sulphate and polyacrylamide) coagulation takes place and the colloidally dispersed particles, which are not decomposed in the biological purification, are removed. The water untreated with the active silt can be purified chemically with alumina and polyacrylamide[99,115].

The sludge lignin isolated has a dark-brown colour, contains up to 98% of moisture which is difficult to remove, and gives rise to stable lumps on drying, which are difficult to grind. The sludge lignin must be dried and the drying process can be carried out twice.

The main part of the precipitate extracted from waste water is a modified sulphate lignin, since, after prolonged treatment with active silt, it undergoes a whole series of processes which alter somewhat its structure[116].

Sludge lignin has a high ash and active silt content. In its activity, the waste water lignin is not inferior to Kraft lignin and can find extensive applications for the reinforcement of rubbers in the technical rubber industry and for the modification of polymers in the plastics industry.

4. The Employment of Sulphate Lignins for the Modification of Polymeric Materials

The applications of sulphate lignins can be divided into three groups: (1) combustion; (2) the use of the surface-active properties of the water-soluble lignin salts; (3) condensation of lignin[24].

In all the industrially developed countries sulphate lignin is used mainly as a fuel in regeneration furnace systems. This application cannot be regarded as normal, because lignin is a valuable chemical raw material and its employment for the generation of power is an example of an uneconomic utilisation of a valuable natural polymer such as sulphate alkali lignin.

Problems concerning the employment of sulphate lignin for the stabilisation of emulsions, in the processing of cement and ceramics, in the dispersion of dyes, pigments, etc., where the surface-active properties of the water-soluble lignin salts are used, and in the preparation of thermoreactive resins in combination with phenols, urea, and other products, have been fairly thoroughly described in the literature. Sulphate lignin can be used to prepare valuable low-molecular-weight products: dimethyl sulphide (the starting material for the manufacture of dimethyl sulphoxide, which is a very valuable solvent), phenolic derivatives more valuable than those obtained from petroleum, vanillin, etc. The possibility, in principle, of using sulphate alkali lignin in the form of liquid self-hardening mixtures in the casting industry, etc. has been demonstrated recently[23–25,48,96,117,118].

Among all the technical lignins, sulphate lignins are chemically the most reactive and have therefore been used for a long time to modify polymers. The majority of investigators believe that chemical bonds may be formed between the lignin macromolcule and the macromolecules of synthetic polymers, although the question of the nature of these bonds

remains open. The oldest and the most familiar application of lignin as a component of polymeric materials involves the reinforcement of raw rubbers. Very extensive studies, published both abraod and in the USSR, have been devoted to this problem[9,15,16,96,119–125].

A distinctive feature of the preparation of lignin-filled rubbers is that, in order to reinforce the latter, lignin is introduced at the latex stage, since the introduction of powdered lignin into dry rubber does not lead to the "reinforcement" effect. It is believed that the reason for this is the binding of lignin particles to one another by hydrogen bonds, which leads to condensation and growth of its particles and prevents the dispersion of the lignin particles during the rolling of rubber[9,119].

The introduction of lignin into rubber at the latex stage greatly complicates and increases the cost of the technology of its manufacture, since the usual method for the preparation of the parent lignin–rubber mixture consists in the dissolution of lignin in an aqueous solution of alkali, mixing of the alkaline solution with the rubber latex, heating the mixture, and the joint coagulation of the rubber and lignin by pouring the mixture into a solution of acid while stirring. The reinforcing effect of lignin is determined by its particle size, which depends on the precipitation conditions and certain other factors[9]. In the parent mixture the lignin is not bound to rubber by chemical bonds. The reinforcing effect of lignin increases appreciably when lignin is precipitated in the presence of sodium silicate[16].

The mechanism of the reinforcement of raw rubbers by sulphate lignin can be accounted for mainly by its surface-active properties and the coagulate is therefore precipitated in the form of fine particles. This leads to the formation of a material with low stress parameters for 300% elongation and a high hardness, so that the lignin-filled vulcanisates exhibit a lower resistance to wear than carbon-black filled rubbers.

In order to eliminate the above defects, the lignin-rubber mixture is treated with polyisocyanates and is used in the manufacture of rubbers for car tyres. The polyisocyanates employed are di- and tri-isocyanates of different chemical structure in amounts ranging from 1 to 10 parts per 100 parts of rubber (dry weight)[126]. The articles obtained from such a composition have improved operating characteristics, in particular the stress corresponding to 300% elongation and the resistance to abrasion increase by a factor of 1.5–2.0 (depending on the content of the additive).

The mechanism of the reinforcement of rubbers by lignin is fairly complex and has not been completely investigated. Apart from the physical explanation, associated with the surface-active properties of lignin, there is a chemical explanation of this phenomenon. The reinforcement of rubbers by alkali lignin can be accounted for by the interaction of the active groups of lignin with the double bonds or active groups of the rubbers—the formation of hydrogen bonds between the hydroxy-groups of lignin and the π electrons of the double bonds of the rubbers[119]. When isocyanates are introduced, the high reactivity of the isocyanate groups promotes the rupture of the hydrogen bonds, which are unable to reinforce the dry lignin and the latter is thus converted into an active series.

Sludge lignin can be used successfully as an active filler and reinforcing agent for polymeric materials[127].

Lignin-filled rubbers can be obtained in two ways: (1) the coprecipitation of lignin and rubber from a lignin–latex mixture by the method indicated above and (2) by introducing hydrated lignin into rubber with the aid of rubber mixing equipment. Both these procedures are technologically complex and uneconomical and have not therefore found extensive industrial applications.

The vulcanisates filled with dry lignin are characterised by a tensile stress σ_t not exceeding 6.0 mN m^{-2}.

Lignin–oil pastes can be used as lignin products isolated from black liquors for the reinforcement of raw and cured rubbers. They are obtained by mixing hydrated lignin, containing approximately 60% of moisture, with a plasticiser (tall oil, pine resin, PN-6 oil), after which moisture is evaporated from the resulting mixture with continuous stirring (the stirring temperature is 60–70 °C). Simultaneously with drying, the lignin is dispersed in the plasticiser, which prevents the agglomeration of the lignin particles and tends to increase the degree of their dispersion. Outwardly, the lignin–oil paste consists of a powder or solid lumps of dark-brown colour, depending on the type of plasticiser. Such a paste can be introduced into rubbers using the normal rubber mixing equipment[123].

Yet another method for the isolation of lignin from black liquors involves its precipitation in the presence of water-soluble additives (low-molecular-weight alcohols, aldehydes, ketones, or emulsifiers) which promote the formation of a highly disperse product. The vulcanisates obtained using these lignins have high values of the tensile stress: $\sigma_t = 16$ and 18 mN m^{-2} respectively.

Dry sulphate lignin is of considerable interest for the filling and modification of thermoplastics in order to obtain frost-resistant polypropylene (PR) compositions and also in the reprocessing of waste from polymeric materials. Studies have been carried out on the creation of composite materials using sulphate alkali lignin based on polyolefins (PO)—materials of the type of poprolin, including preparations based on secondary polyethylene obtained from used articles[17–21,61–67,128–138].

The study of the character of the interaction of the ingredients of the polymer composition under processing conditions is very important for the specific modification of the basic polymer by sulphate lignin (when the content of the latter is up to five parts) and for the determination of the technological regime for the conversion of poprolin materials into articles.

The EPR method is of practical importance for such purposes. It has been established by this method that paramagnetic polypropylene and lignin centres formed at the processing temperatures interact at the interface between the two phases (polypropylene–lignin); it has been shown that the interaction has a radical mechanism[19,64,66,97]. The results agree with data obtained in the study of free radicals in the formation of the carbon black–raw rubber gel. It has been observed that during the rolling of the rubber in the course of its processing, free radicals are formed and interact with the polymer via a radical mechanism[140,141]. An interesting feature of this process is the approximately linear relation between the ratio of the EPR line widths in air and *in vacuo* ($\Delta H_{air}/\Delta H_{vac}$) and the specific surface of the carbon black, which indicates the surface character of the interaction of some of the spins, capable of participating not only in the formation of the carbon black–raw rubber gel but also in the agglomeration of the carbon black particles.

By analogy with data obtained in the study of carbon black by EPR, the concept of c_a/c_0—the relative concentration of the active free radicals on the surfaces of the lignin particles—was introduced for the interpreation of the results in the polypropylene–lignin system and the differentiation of the free radicals present on the surfaces of the lignin particles and responsible for the interaction with the polypropylene; according to the literature[19,129,132], the relative concentration represents the different $c/c_{0\,NaCl} - c/c_{0\,PP}$, where c is the overall concentration of the lignin free radicals at the experimental temperature, c_0 the concentration at room

temperature calculated with a correction for the Curie law, c_0 NaCl the concentration of the radicals R of lignin in the inert NaCl diluent, and c_0 pp the corresponding concentration in the polypropylene matrix. This approach makes it possible to follow the kinetics of the interaction of the paramagnetic centres of lignin and the radicals R of polypropylene at the processing temperatures, to assess its character and to optimise the polymer composition and the optimum lignin content.

In order to improve the operating characteristic of poprolin (to reduce the embrittlement temperature T_{br} and increase the frost resistance), a low-molecular-weight plasticiser dioctyl sebacate (DOS) was introduced into the polypropylene–lignin system, which resulted in the formation of a frost-resistant material—poprolin-1.

It follows from the EPR data that the introduction of DOS into poprolin disrupts the interaction between the paramagnetic centres of lignin and polypropylene, which entails a decrease of c_a/c_0. The attempts to intensify the disrupted interaction by introducing an additional amount of lignin (in excess of the optimum value for the given composition) did not lead to the desired results. Tests showed that the disrupted interaction cannot be restored by introducing fillers of the type of titanium dioxide, which has been stated[24] to be capable of adsorbing lignin, wetting its surface and leading to a more effective dispersion of the plasticiser and lignin in the polymer matrix. Furthermore, the introduction of titanium dioxide prevents the interaction of lignin with DOS, stimulating the interaction of lignin with polypropylene and leading to an enhanced stability of the system[64,65]. These data indicate the possibility of regulating by the above procedures the properties of complex materials important for practical applications.

The study of the rheological characteristics of poprolin-1 showed that the introduction of the optimum amount of lignin (three parts) reduces its fluidity, which entails the transition of the flow curve to the region of the lowest shear stresses compared with the initial polypropylene[19,61,128,139]. This greatly facilitates the processing of poprolin-1, the articles obtained from it being characterised by effective operating characteristics under the conditions of low temperatures (compared with the basic polypropylene) and the range of their utilisation is greatly increased.

One of the procedures in the technology of the processing of plastics designed to increase the quality of the polymeric materials and to increase the useful lifetime of the articles obtained from them is known to involve the introduction of antioxidants in order to suppress oxidation processes occurring under the influence of various factors (high temperatures, solar radiation, etc.). Phenols, as inhibitors absorbing in the ultraviolet, have come to be widely used among antioxidants[142]. The photoreaction of phenols leads to the formation of phenoxy-radicals, which in their turn undergo a photoreaction in the polymer matrix and their subsequent fate depends on their reactivity, temperature, concentration, and the type of polymer matrix[142–144].

In terms of their chemical structure, lignins can be assigned to the class of sterically hindered phenols. On the other hand, the involvement of sterically hindered phenols in radical reactions reduces to the initial abstraction of the hydrogen atom from the hydroxy-group of the phenols with formation of a phenoxy-radical, i.e. the behaviour of the sterically hindered phenol in radical reactions is determined by the properties of the phenoxy-radicals formed. It is known that the O–H bond energy in sterically hindered phenols is somewhat lower than in unsubstituted phenols, which facilitates, on the one hand, the homolytic dissociation of the given bond with formation of phenoxy-radicals, and on the other hand, leads to the formation of thermodynamically more stable species—stable free radicals[144]. The stability of the radicals R formed in the reaction of the antioxidant has a significant influence on the kinetics of the ageing of the polymeric materials, since the probability of the involvement of these radicals, following the enhancement of their stability, in recombination reactions in subsequent processes diminishes, which promotes an increase of the inhibiting effect of the antioxidant. The character of such stability is to a large extent determined both by structure factors (intramolecular stabilisation) and by the interaction of the radicals with the medium (intermolecular stabilisation). The experimental results, showing that lignin or its degradation products can be used as thermostabilisers for polypropylene at its processing temperatures (in excess of 200 °C) and as inhibitors in its photoageing process, may serve as confirmation of the above considerations[64,132,145,146].

However, data have been obtained recently showing that sulphate lignin can be used as a photomodifying additive to polypropylene and that it does not affect its degradation on prolonged irradiation. At the same time it can greatly reduce the efficiency of light stabilisers operating in accordance with an inhibition mechanism, so that, in order to improve the light stability of lignin-containing compositions, it is desirable to introduce additional substances belonging to the class of u.v. absorbers or dyes. Since the ligno-tall product contains simultaneously structure-forming (lignin), reinforcing (aliphatic acid salts), and plasticising (tall oil) substances, it is a complex modifying agent[139].

The application of the ligno-tall substances greatly simplifies the technology of the preparation of frost-resistant polypropylene of the type of poprolin-1 because the necessity for the initial introduction of the scarce and expensive DOS is eliminated.

The application of sulphate alkali lignin in the preparation of compositions based on polyolefins using secondary low-density polyethylene (SLDPE), obtained from worn agricultural sheeting, is of great theoretical and practical interest[20, 21,134–136].

A factor promoting the formation of such composite material (poprolin-2) was the fact that SLDPE is a product activated during use as a consequence of photo-oxidative reactions in the LDPE during the use of the sheeting. The kinetics of the oxidation of the LDPE depend to a large extent on the degree of branching of the polymer and the oxidation proceeds via the formation of polymeric hydroperoxides (POOH) and ketones with the possible occurrence of radical reactions in the photodecomposition of ketones via a Norrish type I mechanism[147,148]. At the same time an additional amount of radicals R are formed in the SLDPE, their concentration being somewhat greater than in LDPE and lower than in polypropylene[19]. As a result of the formation of an additional amount of free radicals in the secondary polyethylene matrix, the effect of the interaction of the polymeric components in poprolin-2 (SLDPE and polypropylene) with lignin is much stronger, which increases the stability of the composition as a result of the improvement of the operating stability of the system.

Materials of the type of poprolin have been successfully converted into articles of extrusion (film materials, including coextrusion films based on moderate-pressure polyethylene, tubes, and sheets), by casting under pressure (transport packing capable of repeated use for branches of industry manufacturing food products), and by mechanothermomoulding and rotation moulding (large packing for various branches of the national economy)[131,133,137].

A distinctive feature of articles made of poprolin materials is their effective physicomechanical and operating characteristics (compared with various polyethylenes and even polypropylene) and the lower intrinsic cost of the articles obtained from them. The poprolin materials are more susceptible to technological procedures and have a better capacity for being worked compared with the basic polymer. The use of poprolin provides the national economy with a significant economic gain by increasing the useful lifetime of articles in the course of their employment, and promotes the rational employment of natural resources, protection of the environment, and the expansion of the reserves of a scarce primary polymeric raw material as a result of the employment of a secondary raw material.

The study of the behaviour of lignin in the modification of wood by synthetic polymers is of interest because it is one of the high-molecular-components of wood. The possibility of radiation grafting onto isolated lignin of various synthetic polymers, for example styrene, methyl methacrylate, and acrylonitrile has been demonstrated[149–154]. It has been established that the radiation-chemical modification of wood with styrene involves the cross-linking of lignin and polystyrene, in which stable free radicals play an appreciable role[155].

Studies of the polymerisation of styrene with hydrochloric acid lignin and Kraft lignin with chemical and radiation initiation have been carried out by non-Soviet workers[150,155,156], who, with the aid of model lignin compounds (guaiacol, 2,6-dimethoxyphenol, and isoeugenol), discovered its inhibiting effect on the polymer. The graft copolymerisation of lignin and styrene takes place as a result of the transfer of the chain of the growing polymer radicals to the lignin units containing phenolic groups, which have an inhibiting effect on the kinetics of the process, resulting in its retardation, which entails the formation of a graft copolymer with a reduced molecular weight.

Sulphate lignin has an analogous effect on the thermal initiation of styrene in dimethyl sulphoxide in the presence of chemical initiators[157]. A considerable increase of the inhibiting effect of lignin in the presence of oxidants (for example, atmospheric oxygen), owing to the formation of quinonoid structures for both chemical and radiation methods of initiation has been noted.

The graft copolymerisation of various monomers with wood lignin leads to a new way of creating mixed composites with a graft structure as a result of the mixed chemical combination of natural and synthetic polymers possessing a valuable set of properties.

According to structural ideas, grafting can occur on the surface of the polymer particle (surface grafting) and within it (block grafting), which depends on the process conditions. By creating conditions for grafting via one procedure or another, it is possible to regulate within wide limits the properties of the resulting composite materials[158].

Like hydrolytic lignin, sulphate lignin can be used for condensation with phenols in order to obtain lignophenol-formaldehyde resins. In the polycondensation reaction the phenol adds to lignin via a ring hydrogen atom but not a hydroxyl hydrogen atom, which follows from the solubility of phenol-lignin in alkali. The introduction of a third component (formaldehyde) makes it possible to obtain fusible and alcohol-soluble resins whose properties are analogous to those of industrial products[25].

Latvian investigators suggested that hydroxypropylated lignins (HPL) be obtained on the basis of modified lignoorganosilicon oligoethers and epoxypropane[159], which constitutes an extremely promising application of technical lignins. A method for the preparation of polyurethane foam materials (on the basis of HPL) has been developed; HPL can be used as fillers (based on technical lignins) for plastics.

There exist data concerning the utilisation of modified sulphate and sulphite lignins for the preparation of a composite friction material with up to 15 wt.% of lignin[160].

A new and promising application of all types of technical lignins in the light of the fulfilment of resolutions concerning the rational employment of natural resources and the protection of the environment involves the development of highly filled polymeric materials based on lignin—lignoplastics. This task is extremely complex and laborious, since it requires very extensive scientific and technological investigations and also the creation of industrial comminuting equipment. However, a realistic basis for its successful fulfilment already exists.

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Use of Porous Polymer Sorbents for Concentrating Traces of Organic Compounds from Gases or Liquids

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The advantages and disadvantages of the adsorption method of concentrating organic trace impurities of various types from air or from liquids are discussed. The main types of sorbent currently used are examined, and their adsorption characteristics are compared, with special emphasis on porous polymer sorbents. The special features of these polymers when used as concentrators are stressed, and interrelationships are established between the characteristics of the sorbents and their effectiveness in the sorption of different classes of organic compounds, and between their adsorption capacity (or percentage extraction) and the concentration conditions. Problems in the storage of samples concentrated on polymer sorbents are discussed. Some examples of the practical use of polymer sorbents for concentrating organic trace impurities from air or from liquid media are given. 106 references.

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I. INTRODUCTION

The analysis of air contamined by industrial and by domestic waste products and the analysis of natural waters and effluents are among the most important problems in the wide-ranging efforts now being devoted to the protection of the environment. Information on the relative amounts of trace impurities (especially in the case of toxic substances) is needed both in theoretical studies and in the control of industrial practices. Chromatography is now the main method of impurity analysis for air and water[1,2]: its most important advantages are its high selectivity and the wide choice of sorbents and of separation conditions, which make the method ideally suitable for monitoring the composition of the environment.

Because of the relatively low concentration of organic impurities in air, water, and biological fluids most of the chromatographic methods used for impurity detection rely on a preliminary concentration stage. The main steps in the determination of trace impurities† in air and in water are the same: 1) collecting and storing the sample, 2) concentrating the components, and 3) chromatographic analysis. However, depending on whether the sample is air or water, the stages differ in a number of important aspects, discussed (for example) in Refs.1–5.

II. MAIN METHODS OF CONCENTRATING TRACE IMPURITIES OF ORGANIC COMPOUNDS

The following methods have been used for the pre-concentration of organic trace impurities in air: liquid extraction, freezing, chemical trapping of the components, and adsorption of the impurities by sorbents. In the case of water samples additional methods are available, including thermal methods (based on changes in solubility on heating), vacuum and thermo-vacuum methods (based on gas evolution at reduced pressure), and studies of the equilibrium vapour phase.

The extraction method requires high-purity extracting agents and offers only a moderate sensitivity. Liquid–liquid extraction is usually organised as a cyclic process. It is applicable mainly to samples with relatively high concentrations of impurities and relatively low volumes, since large-volume samples make the method excessively laborious. The most commonly used extractants are methylene chloride, chloroform, hexane, and carbon disulphide. The efficiency and speed of the extraction depend on the distribution coefficient of the substance between water and the organic solvent, and on the area of contact between the two phases. The cyclic process is not very effective even when the distribution coefficient is relatively high, and a continuous (or multi-stage) extraction process is now recommended for effective extraction[6]. The main shortcoming of the extraction method is the need to introduce a new solvent, which complicates the subsequent gas-chromatographic analysis. The scrubbing of gas samples with organic solvents has the same disadvantages as liquid–liquid extraction.

When freezing is used as a method of concentrating impurities it is difficult to avoid the incorporation of the wanted impurity in the growing ice crystals. Furthermore, the presence of large amounts of salts in the samples introduces additional complications in the freezing method.

Chemical trapping of the components has only a limited application. The use of thermal and thermo-vacuum methods is difficult in the presence of mechanically entrained contaminants and of surface-active compounds. Decomposition and hydrolysis of the components during desorption (by raising the temperature) must also be guarded against.

Organic compounds dissolved in water are often determined by analysing the equilibrium vapour phase[7,8]. The method involves heating the liquid sample in a closed vessel and studying the composition of the vapour phase in thermodynamic equilibrium with the liquid. Several variants have been described. In the simplest, the equilibrium vapour phase is sampled with a hypodermic syringe, from which the sample is transferred directly to the chromatograph[9]. However, if the organic compound is present in trace amounts in the water, direct sampling of the vapour is seldom adequate, because of the limitations imposed by the sensitivity of the chromatographic detector.

† The trace impurity range corresponds to concentrations between 10^{-1} and 10^{-7} % by volume or weight.

In a method recently proposed[10] for extracting organic impurities from water 5–10 ml samples are forced in air pressure through a special column (called the concentrator) consisting of a glass tube with capillary contructions, which assists the transfer of the impurity to the vapour phase, from which it is injected into the chromatograph by a stream of air. The main shortcomings of this method is its limited application (to high-boiling substances).

The most promising of the methods of concentrating trace impurities listed above is the adsorption method, in which a column packed with a porous sorbent is used as the concentrator. The experimental procedure is the following: a known volume of gas or liquid is passed through a column 2–4 mm in diamter and 2–5 (or up to 50) cm long, packed with the sorbent, under controlled flow-rate and temperature conditions. The organic compounds present in the air (or water) sample are retained and accumulated in the column: the concentrator column acts as a chromatographic column operated at room temperature or below, and the sample of air or water acts as the mobile phase.

The adsorbed substances are recovered from the concentrator by extraction with an organic solvent, or by thermo-desorption. Both these methods are widely used in practice, though the extraction variant causes dilution of the sample with a corresponding loss of analytical sensitivity. The thermo-desorption method is therefore preferred for compounds stable at high temperatures, as it is both simpler and less time-consuming. The choice of the desorption method assumes thermal stability of the sorbent: it should be possible to desorb the impurity completely and without decomposition of any component of the mixture at a temperature chosen according to the boiling points and chemical nature of the components. The thermo-desorption method can form the basis of a simple and fully automated system for concentrating trace impurities from air[11].

However, even in the thermo-desorption method the detection limit may be affected by the spreading of the chromatographic bands of the impurity components being transferred to the analytical column. Therefore, in order to increase the analytical sensitivity, we must optimise the transfer of the concentrated impurities to the analytical column. One way of doing this is to insert an additional trap cooled in liquid nitrogen (capillary loop) after the concentrator; this makes the injection of the concentrated sample even more compact[11–13]. An alternative method is to raise the temperature of thermo-desorption of the impurities, but of course this method makes even more stringent demands on the thermal stability of the chosen sorbent. The desorbed impurities are analysed gas-chromatographically in analytical columns (packed, or capillary). The chromatograph is combined with a mass-spectrometric detector to identify the peaks resolved by the analysis.

Interesting results have been obtained by combining the analysis of the equilibrium vapour phase and the adsorption method. It is found in practice that the sensitivity of the analysis is substantially increased by concentrating the substances present in the vapour phase on columns packed with sorbent. Thus a modification[14] of a system previously described[10] (by inserting a Polisorb-1 column to remove the impurities from the vapour phase) has enabled alcohols, ketones, aldehydes, and esters to be detected in the effluent waters of hydrolysis and alcohol production plant.

One of the variants of the combined method (analysis of the equilibrium vapour and pre-concentration by adsorption) is to examine the vapour over the heated liquid sample swept by a stream of inert gas[15,16] into an adsorption concentrator. Another variant (the gas-phase extraction method[17,18]) relies on bubbling an inert gas through the water sample at a known rate (usually 40–80 ml min^{-1}). The organic impurities pass into the gas phase and are thus gradually removed from the water. The distillation time is 1–3 h, depending on the flow rate of the gas and on the volume and temperature of the sample vessel, controlled by a regulator between room temperature and 70–80 °C. The dynamical nature of this method ensures a high level of extraction at room temperature for substances boiling below 150 °C. If additional concentration of the impurities is needed a water-cooled condenser (to remove the water entrained by the gas flow) and a concentrator filled with adsorbent are inserted into the gas outlet stream[6].

III. CHOICE OF SORBENT FOR PREPARING CONCENTRATOR COLUMNS

The choice of sorbent for the concentrator column depends mainly on the nature of the compound for analysis, and is determined by the intermolecular interactions in the sorbent–sorbate system (as in any other chromatographic process).

The sorbent should have an adequate capacity for the given substance. The adsorption should be reversible, i.e. without chemical changes. Furthermore the sorbent should be thermally stable and its affinity for water should be low (especially for the analysis of solutions and moist gases). If the capacity of the sorbent is insufficient for all the components of the mixture several sorbents can be used instead of a single sorbent[19,20], and placed in the same concentrator.

The sorbents most commonly used for concentrating trace impurities include activated carbon, graphitised thermal black, molecular sieves (including carbon-based sieves), various grades of silica gel and aluminium oxide, sorbents for gas–liquid chromatography[3,21], and porous polymer sorbents.

Activated carbon has a high adsorption capacity, which allows this sorbent to be used in small amounts, and it is also thermally stable. However, it holds the trace impurities very strongly, making them difficult to desorb. Thus the use of carbon may lead to incomplete recovery of the impurities (due to the irreversibility of the adsorption) accompanied by the appearance of spurious peaks (due to impurities already present in the carbon)[22]. Effective removal of low-molecular-weight compounds (for example, ethylene and methylene chlorides) requires strong cooling of the concentrator, which is not always convenient[4]. Furthermore activated carbon reacts with several organic compounds (especially with sulphur compounds). Desorption from carbon usually requires extraction with organic solvents. Transfer of the concentrated substances to the analytical column can be achieved also by thermo-desorption, but often the temperature required is unacceptably high because of the very fine porous structure of carbon.

The use of carbon molecular sieves and graphitised blacks (Carbopaks, Carbochroms, Carbosieves, Spherocarbs) for concentrating traces of organic compounds is limited by the irreversible sorption of many compounds on these sorbents and by the high reactivity of the sorbents. Their main disadvantage, as with the activated carbons, is the need to use organic solvents for the desorption of the concentrated impurities (causing dilution of the sample and loss of analytical sensitivity) or alternatively to use elevated desorption temperatures (causing decomposition of the organic compounds).

Silica gels are used for concentrating hydrocarbons with a C_3 or higher carbon skeleton, as well as organic compounds of other classes. The adsorbed substances are usually

desorbed by extraction of (very unusually) by thermodesorption. Among the shortcomings of silica gel as an adsorbent for concentrating trace impurities we should list incomplete recovery of volatile hydrocarbons, adsorption of water vapour from the air sample for analysis, and a tendency towards irreversible sorption of easily polymerisable unsaturated compounds and of compounds chemically reactive towards silica gel (for example, organic bases).

The sorbents used in gas–liquid chromatography (i.e. carriers coated with a stationary phase) are unsatisfactory in the following respects[23]: 1) possible reaction between the compound and the stationary phase (for example, Dexsil-300 and alkalis), and 2) contamination of the sample for analysis by impurities from the liquid phase.

IV. POROUS POLYMER SORBENTS IN THE ADSORPTION METHOD OF CONCENTRATING TRACE IMPURITIES

The porous polymer sorbents Porapak Q, P, N, Tenax GC, Chromosorb (100 series), Amberlite XAD, Polisorb 1, 10, etc. are now widely used for concentrating impurities from air and water. They offer a high adsorption capacity towards many organic substances and a rapid concentration of the impurities, shortening the analysis time of an air sample (say) to 10–20 s.[24] They have a low sorption capacity for water, which is often present in analytical samples (especially in the analysis of the equilibrium vapour phase), and they are chemically inert and thermally stable. Concentration on porous polymer sorbents can be combined with direct thermal desorption (instead of liquid extraction) to transfer the impurity from the concentrator to the gas chromatograph. This offers an enhanced analytical sensitivity and avoids possible interference by the solvent. The concentration of trace organic impurities on porous polymer sorbents is now widely used in analytical practice including impurity analysis in environment protection studies, in industrial hygiene, and in biochemistry and medicine[15,25–30].

1. Main Characteristics of the Sorbent

The sorbents most commonly used for concentrating trace impurities are listed in Table 1. In most cases the sorbent surface is hydrophobic, but XAD-7, XAD-8, the Spherons, and Amberlyst A-26 are hydrophilic. Dressler has pointed out[5] that hydrophobic non-polar sorbents are more effective for concentrating non-polar compounds, whereas for polar compounds hydrophilic adsorbents should be used: the adsorption capacity of the hydrophobic sorbents increases as the polarity of the compound decreases. The particle size of the polymer sorbents used at present is 25–50 or 35–60 mesh. However, an increased sorption capacity can be achieved[6] by using a smaller fraction (80–100 mesh) of the sorbent particles.

The fairly wide choice of types of synthetic polymer sorbent (differing in structure and in surface-chemical properties) which can be combined within the same concentrator explains the successful use of these materials for concentrating organic trace impurities of different classes, with boiling points covering a wide range. Dynamical enrichment on porous polymer sorbents is subject to the following limitations: 1) incomplete adsorption of molecules of low molecular weight, and 2) the appearance of spurious peaks during desorption, due to impurities in the initial polymer. The first of these shortcomings can seriously limit the application of the method, but it can be overcome by an appropriate choice of polymer sorbent. The influence of the second factor can be lessened by a thorough preliminary purification of the sorbent. Hence the purification procedures applied to the sorbents are among the most important aspects of the practical application of porous polymer sorbents to the concentration of trace impurities.

Table 1. Polymer sorbents for concentrating trace impurities[5,94].

Sorbent	Composition of polymer	S_{sp}	d, Å	t, °C
Amberlite XAD-1	copolymer of styrene and divinylbenzene	100	200	250
Amberlite XAD-2	ditto	290—330	85—90	250
Amberlite XAD-4	"	750	50	250
Amberlite XAD-7	copolymer of methyl methacrylate and divinylbenzene	450	80	150
Amberlite XAD-8	ditto	140	250	150
Amberlyst A-26	anion exchange resin containing trimethylamino groups	25—30	—	—
Ostion SP-1	Copolymer of styrene and divinylbenzene	350	86	250
Polisorb-1	ditto	200—250	130	250
Polisorb-10	polyvinylbenzene	300—350	—	250
Polisorbazol	copolymer of *N*-vinyl-3(5)methylpyrazole and ethylene glycol dimethacrylate	300—400	100	280
Polisorbimid-1	copolymer of pyromellitic dianhydride and diaminodiphenyl ether	40—60	1000	450
PFKh	polyphenylquinoxaline	30—50	1600	300
Porapak N	copolymer of styrene, divinylbenzene, and vinylpyrrolidone	500—550	75	200
Porapak P	copolymer of styrene and divinylbenzene	100—200	—	250
Porapak Q	copolymer of ethylvinylbenzene and divinylbenzene	630—840	75	250
Sinachrom	copolymer of styrene and divinylbenzene	520—620	45	250
Spheron MD 30/70	copolymer of methyl methacrylate and divinylbenzene	320	—	230
Spheron SE	copolymer of styrene and ethylene dimethacrylate	70	—	280
Tenax GC	poly(2,6-diphenylphenylene oxide)	19—30	1400	350—375
Chromosorb-102	copolymer of styrene and divinylbenzene	300—400	85—95	250
Chromosorb-105	copolymer of the polyaromatic type	600—700	—	200
Chromosorb-106	cross-linked polystyrene	700—800	—	250

Symbols. S_{sp} is the specific surface, d is the average pore diameter, t is the upper limit of the working temperature range.

2. Preparation of Sorbents for Concentrating Impurities

Preliminary purification of the sorbents removes the main impurities and improves the reproducibility of the analytical results. The polymer sorbents can be prepared in a form suitable for the experiment by the following methods: conditioning in a stream of oxygen-free carrier gas at high temperature (e.g. for Porapak, heat treatment at 225–250 °C in a stream of carrier gas for 12–24 h is recommended[5]), degassing at high temperature in a vacuum, or extraction with organic solvents. The latter method is used most often with sorbents of the Amberlite type, used for concentrating impurities in water. Thus Junk and co-workers[31] recommend the following pre-treatment of Amberlite XAD-2 and XAD-4: wash the sorbent particles several times with water or 0.1 *N* NaOH solution, decant them from methanol, and extract them in a Soxhlet apparatus with methanol, acetonitrile, and diethyl ether (8 h in each solvent). After this pre-treatment the sorbent is stored in a glass vessel under methanol. The

concentrator trap is prepared by filling the column with the purified sorbent (added as a suspension in methanol) and washing the packed layer several times with distilled water.

Lower levels of detection of organic impurities in drinking water have been acnieved[32] by adopting a method of purification of the XAD-2 resin which includes successive washings with methanol, diethyl ether, and water. It is stressed that this preliminary purification prevents the formation of decomposition products of the sorbent in contact with water, such as alkanes from $n\text{-}C_{10}H_{22}$ to $n\text{-}C_{24}H_{50}$.[32]

When Tenax GC is used as the sorbent in gas chromatography a conditioning treatment in nitrogen (1 h at room temperature and 1 h at 350 °C) is recommended[33]. Tenax samples for packing concentrator columns have been conditioned at 350 °C for 30 min [34] or for 3 h, followed by 12 h at 200 °C.[35]

3. Sorption Capacity of Porous Polymer Sorbents

The most important factor in the successful application of trace impurity concentration processes is an adequate sorption capacity of the sorbent at the concentration temperature. The sorption capacity for each sorbate (g g^{-1} of sorbent) can be determined from measurements of the sorption front[36]:

$$\alpha = \frac{(t - t_M) F}{W_s} \cdot c$$

where α is the dynamical adsorption capacity for the given sorbate (g g^{-1}), t is the time needed to saturate the sorbent to break-through of the sorbate (s), t_M is the retention time of the gas which is not sorbed (s), W_S is the mass of sorbent (g), F is the flow rate of the carrier gas ($cm^3\ s^{-1}$), c is the concentration of sorbate in the carrier gas (g cm^{-3}), and $(t - t_M)F/W_S$ is the volume of carrier gas containing sorbate at concentration c needed to saturate 1 g of sorbent at the chosen concentrator temperature (293 K).

Comparative studies of the adsorption capacity of several polymer sorbents (Tenax, Porapak P and Q, Amberlite XAD, and Chromosorb 101 and 102) towards volatile organic compounds have been reported[15,20,37,38]: alcohols, ketones, organic acids, nitrogen and chlorine compounds, saturated and aromatic hydrocarbons. The capacity of a sorbent for a given compound was shown to be determined by the nature of the sorbate as well as by that of the sorbent. On the whole, polar compounds are sorbed more effectively by polar polymer sorbents, for example XAD-7 and XAD-8 Amberlites. In non-polar polymer sorbents (e.g. Porapak P, XAD-1, XAD-2, etc.) the adsorption increases with the molecular weight of the sorbate and with decreasing polarity of its molecules.

If the chemical nature of the sorbent is kept constant the adsorption capacity is determined by structural characteristics (specific surface area and porosity). Experimental data on the adsorption capacity for volatile organic compounds have led to the classification of the porous polymer sorbents in the following sequence[37].

$$\text{Tenax} \cong \text{XAD-1} < \text{Porapak P} \ll \text{XAD-2} < \text{Porapak Q} < \text{XAD-7} < \text{XAD-4}$$

For Tenax and the XAD-7 and XAD-4 Amberlites[38] the lowest adsorption capacity is observed with cyclohexane, methanol, and ethanol. The concentrator properties of XAD-7 are the most favourable of this group of three sorbents[38], but nevertheless most of the recent work on the concentration of volatile organic compounds (especially from air) has been done with Tenax because of its exceptionally high thermal stability.

The capacity of a sorbent towards a given compound determines the break-through volume, i.e. the volume of gas or liquid which passes through the sorbent before the appearance of the substance of interest. The break-through volume is treated by many workers as synonymous with the retention volume V_R. However, in general the break-through volume can be smaller than the retention volume because of the correction for the concentration conditions[39].

The break-through volume for the polymer sorbent Tenax has been determined[39] by passing a stream of gas containing the impurity through a trap packed with the sorbent and connecting the outlet to a flame-ionisation detector (direct measurement); it has also been calculated theoretically[40] from the retention volumes and the number of theoretical plates in gas-chromatographic measurements (indirect measurement).

The dependence of the break-through volume on the basic concentration conditions (flow rate of the mobile phase, concentrator temperature, concentration of the impurity and of water vapour in the gas stream) has been investigated. The break-through volume in Tenax was found to be strongly dependent on the velocity of the mobile phase. Thus for a stainless steel concentrator (75 mm × 4.5 mm) containing 0.13 g of Tenax which had been pre-heated at 250 °C for 16 h the optimum flow velocity was 50 ml min^{-1}. The impurity concentration and the temperature also have an effect on the break-through volume. To a first approximation V_R increases two-fold for a decrease in temperature of 10 K. The break-through volume in Tenax is almost independent of the water content of the air sample. This is confirmed by measurements[41] of the specific retention volumes of several model compounds (methanol, ethanol, propanol, ethyl acetate, acetone, and benzene) on Tenax in a carrier gas saturated with water vapour. The difference between retentions in the presence and in the absence of water vapour was shown to be ±10%.

Thus Brown and Purnell conclude[39] that a flow rate of the mobile phase of 500–600 ml min^{-1}, a concentration of the impurity vapour of 100 ppm, a concentrator temperature of 20 °C, and a relative humidity of 95% the break-through volume in Tenax is not less than 50% of the measured retention volume of each compound. Hence they recommend determining the retention volume of the organic compounds experimentally at 20 °C and taking 50% of this quantity as the safe volume for a number of stated assumptions (i.e. the volume of contaminated air which can be passed through the adsorbent before break-through). Other workers[42] take the safe volume as 1/3 of the measured retention volume.

The capacity of the packed column is calculated from the parameter V_R at the concentrator temperature (usually room temperature or below). Since V_R is often determined gas-chromatographically at higher temperatures, linear extrapolation of the retention volumes to room temperature[20] is needed. The possibility and the validity of this extrapolation for polymer sorbents have been examined[43] by using $CHCl_3$, CCl_4, and CH_3CCl_3 as sorbates. The retention volumes determined gas-chromatographically at room temperature were compared with those obtained by extrapolation, and in this way the sorption capacity of the column (filled with polymer sorbent) extrapolated from measured retention volumes was shown to differ somewhat from the true value. The discrepancy is different in different systems, and is a characteristic of the particular system. For example, the capacity of Porapak Q columns for all these halogen compounds is higher than the extrapolated value. Nevertheless the extrapolation of V_R to room temperature is often used in practice because of the simplicity of the calculation.

4. Percentage Extraction of the Compounds for Analysis

The parameter which most accurately characterises the ability of a sorbent to adsorb a compound during the concentration stage and to desorb it during treatment with solvents or when heated to a suitable temperature is the percentage extraction, defined as the ratio of the quantity of substance found in the model sample of air or water after concentration to the quantity of the same substance originally present in the sample (expressed as a percentage). At least two effects can cause low percentage extraction: 1) incomplete adsorption, when a substantial proportion of the trace impurity is lost in the stream of mobile phase, and 2) strong adsorption, when the substance is incompletely desorbed by heating the concentrator. When porous polymer sorbents are used to concentrate the trace impurities from water or air the percentage extraction of organic substances is relatively high. Thus for Amberlite XAD-2 and XAD-7 used in concentrating water samples the percentage extraction of most of the common organic substances (including aliphatic and aromatic hydrocarbons, ketones, ethers, organic acids, phenols, nitrogen and halogen compounds, pesticides, and herbicides) is 75–100%, [5] and in the concentration of impurities from air on Tenax the percentage extraction for hexane, light petroleum, biphenyl, acetone, diphenylamine, and *o*-cresol is 90% with a standard deviation of 5%. [44]

It has also been shown[45–49] that the percentage extraction depends on the particle size of the sorbent, on the concentration of the components in the sample, on the flow rate of carrier gas through the layer of sorbent, on the size of the column, and (in the case of water analysis) on the pH of the sample, on the polarity of the eluent, and on the presence of electrolytes. For example, when a finer fraction of XAD-2 Amberlite (85–120 instead of 60–80 mesh) was used for concentrating chlorinated insecticides a higher percentage extraction was obtained[47]. It has been pointed out[46] that the percentage extraction can often be improved by using a 60 mm × 10 mm column instead of a 30 mm × 10 mm column, while the adsorption of herbicides on XAD-2 Amberlite is relatively unaffected by changes in flow rate from 2 to 10 ml min^{-1}. A flow rate of the water sample of 5 ml min^{-1} was found to be the optimum, but increasing the flow rate still further (from 10 to 32 ml min^{-1}) lowered the percentage extraction. It was also shown[46] that the percentage extraction of organic acids and phenols is related to the dissociation of these compounds and therefore depends on the pH of the solution. In an acid medium the percentage extraction of acids and phenols is markedly higher, and acidification of these samples to pH 2 with HCl is recommended.

5. Permissible Storage of the Concentrated Impurities in the Concentrator

Trace impurities from air or water can be concentrated in the field and stored in the concentrator (trap) until they can be taken to the laboratory for analysis. The use of polymer sorbents in concentrators helps to overcome the difficulties presented by the lengthy storage of concentrated compounds. A possible reason is the relative inertness of the surface of these sorbents, which ensures that the composition of the sorbed organic compounds remains constant, as shown by an analytical study[12,50] of a series of volatile compounds concentrated on Tenax. It has also been shown[50] that the percentage extraction of substances from the concentrator is unaffected by one week's storage of the concentrator at 0.4 or at 20 °C. Goldberg and Sandler[12] mention that a previously conditioned Texan column retained its good adsorption properties throughout the investigation (several weeks), and no spurious peaks were noted in the chromatograms. Keeping the concentrator (containing the concentrated impurities) for 90 days gave a chromatogram indistinguishable from that obtained by carrying out the concentration and the desorption on the same day.

The possibility of lengthy storage of concentrated impurities without change in qualitative or quantitative composition has been reported[51] also for polyurethane sorbents and sorbents of the Amberlite type

V. THE USE OF POROUS POLYMER SORBENTS IN SOLVING CONCENTRATION PROBLEMS

1. Concentration on Tenax

Tenax is the porous polymer sorbent most widely used for concentrating trace impurities[24,28,35,52–63]#. Its main advantages over all other similar sorbents are a high thermal stability (up to 375 °C) and a low "noise" level during thermo-desorption.

The sorption capacity of Tenax towards organic compounds of different types has been shown[50,64] to be high: an important attribute in the analysis of biological fluids, perfumes, and atmospheric pollution. Furthermore the sorption of test substances on a Tenax fore-column was found to be unaffected by the presence of water vapour. Losses of trace impurities during concentration from the 10^{-6}–10^{-9} g ml^{-1} level, and the consequent errors in the quantitative determination, were shown[64] to be due in many cases to the irreversibility of the adsorption on Tenax, and to depend on the composition of the mixture and on the concentration conditions. The sensitivity of the determination of trace impurities can be improved by blocking the Tenax active centres. Thus a preliminary injection into the column of a few microlites of octan-1-ol produces a large increase in the peak area (and a corresponding lowering of the detection threshold) for tributylamine, 2-ethylphenol, butyrophenone, etc. [64]

Bunch and Pellizzari[65] examined the possibility of chemical changes in unsaturated compounds (but-2-ene and cyclohexene) during concentration on a Tenax surface in the presence of traces of Br_2 and Cl_2 in the air sample. They showed that under these conditions the sorbent surface can induce reactions leading to the formation of halogenated hydrocarbons. These reactions can be suppressed by inserting a filter of glass wool soaked in sodium thiosulphate in the gas stream before the concentrator. However, in general the Tenax surface is acceptably inert, giving concentration without significant changes in chemical composition[52–63].

The retention volumes of many organic substances on a Tenax column have been determined[66] at 100–200 °C and extrapolated to 25 °C. The conclusion was that Tenax can be used most successfully for concentrating compounds containing more than seven carbon atoms. For lighter molecules the carbon adsorbent Ambersorb XE-340 is recommended[66], though Porapak sorbents are also usable[20].

The sorption characteristics of Tenax and Carbopak in the concentration of trace impurities of different classes from air contaminated with industrial effluent gases[52] has been published. Carbopak B, a graphitised thermal black with a specific surface of 90 m^2 g^{-1}, can be used at practically any

Tenax is a linear polymer of 2,6-diphenylphenylene oxide with a molecular weight of (0.5–1.0) × 10^6, a specific surface of 19–30 m^2 g^{-1}, and an average pore diameter of 1400 Å.

temperature. When compared in terms of the percentage extraction of a series of organic compounds the adsorption characteristics of Tenax and Carbopak B are generally similar, but sorption properties specific to each adsorbent can also be detected. Thus benzene and n-hexane are fully retained by Carbopak B, but they pass through Tenax (in which their percentage extraction is 35 and 20% respectively). Similar effects are observed for the alkanes from n-pentane to iso-octane. Acetone is most effectively retained by Tenax, but butanol and diethylamine should be concentrated on Carbopak B. On average, for all the classes of organic compounds so far examined, the percentage extraction is 83% on Carbopak B and 75% on Tenax. The use of Carbopak B for the absorption of the C_4–C_5 hydrocarbons and of Tenax for organic compounds with a greater number of carbon atoms has been recommended[52].

A concentrator trap containing 2 cm^3 of Tenax of 30–60 mesh particle size has been used[15] to extract impurities for air and water in the analysis of perfumes and biological fluids. The compounds held on Tenax were desorbed at 300 °C, and the sorbent was regenerated at 375 °C. Gas-chromatographic analyses were carried out on a capillary column.

Columns 15 cm long and 1 cm in diameter containing 2.5 g of Tenax (60–80 mesh) have been used[44] to concentrate trace impurities from air. A 5 litre sample was passed through the concentrator at 0.5 cm^3 min^{-1} and 20 °C. The concentrated substances were transferred to traps (stainless steel tubes of 1.6 mm inside diameter) cooled in liquid nitrogen. Desorption from the trap involved heating the tubes to 300 °C. The percentage extraction of individual organic compounds from model mixtures was ~90% on average.

A preliminary concentration of the trace impurities was used to analyse the volatile components in the cabin of the orbital station Skylab-4 at various times during the mission[11]. More than 300 components were detected gas-volumetrically, and 107 0f these were identified on a mass spectrometer (Freons, siloxanes, hydrocarbons, benzene derivatives, and other compounds with molecular weights between 60 and 500). The concentration was carried out in a Pyrex tube (50 mm × 10 mm) filled with Tenax (60–80 mesh). The procedure included thermo-desorption, transfer of the sample by a gas stream to a trap cooled in liquid nitrogen, and temperature-programmed gas chromatographic analysis.

An analysis[67] of cigarette smoke in air relied on a preliminary concentration in a column (115 mm × 5 mm) packed with Tenax (60–80 mesh) and Carbopak BHT, followed by thermo-desorption at 270 °C into a capillary column coated with OV-101 (25 or 55 m × 0.35 mm). The smoke was found to contain a very wide range of compounds, from low-boiling gases to almost involatile polymers and other high-molecular-weight compounds. The main constituents of smoke are aliphatic and substituted aromatic hydrocarbons.

A special study of concentration problems in the analysis of complex mixtures of organic compounds in water at and below the 1 ppm level has been described[12]. The method included direct injection into the system of a 100 μlitre sample of the water, removal of the water in a condenser at 0 °C, concentration of the trace impurities in a small fore-column (2 cm × 1 mm) cooled in solid CO_2 and filled with Tenax (35 to 60 mesh), and gas-chromatographic analysis of the impurities in a capillary column with a flame-ionisation detector. The method gave very good reproducibility (mean standard deviation 5–6%). Only 4 min were needed for the preparation of the sample for analysis.

A recent review[68] is devoted to the apparatus for extracting trace impurities from water or air and to the methods of concentration on Tenax. The following systems are discussed in detail: hexachlorobutadiene in air (at the 20 ppb level), glycol esters in water (500 ppb), chlorobenzenes in water (3–8 ppb), chlorobenzenes in methylene chloride (100 ppb), and phenols and soluble aromatic compounds in water (300 ppb).

An interesting method of analysis for complex mixtures containing low-boiling gases, water, and organic compounds has been described[69]. It relies on the reversibility of the adsorption of the vast majority of organic compounds on Tenax, whereas water and the light gases pass through the column without being sorbed. A short fore-column containing 0.3 g of Tenax, placed in front of the main column, is used to sorb all the organic compounds from the mixture, while water and the gases pass into the analytical column filled with Chromosorb 101 or Porapak QS. After elution of the water and gases the organic compounds are thermally desorbed from the Tenax into a second analytical column filled with 10% XE-60 on Chromosorb WHP. A system of valves allows the two parts of the analysis to be carried out with a single sample injector and a single detector.

2. Concentration on the Porapak, Chromosorb, and Spheron Types of Porous Polymer Sorbent

Porous polymer sorbents other than Tenax has been used[5,38] for concentrating trace impurities from air, water, and organic liquids. Chromosorb-105 was used[70] to concentrate trace impurities from the equilibrium vapour phase of organic liquids, from air, or from water. Volatile compounds from juices, biological fluids, wine, and brandy were concentrated, analysed on a capillary column, and identified mass-spectrometrically. The preliminary activation of the concentrator filled with Chromosorb-105 consisted in heating the tube at 225 °C for 12–24 h in a nitrogen stream (10 ml min^{-1}).

In the determination of trifluorochloromethane, chloroform, and other chlorinated compounds in air from Michigan the samples were pre-concentrated[71] on Porapak N, and sulphur compounds in town gas from Nogai (Japan) were pre-concentrated[72] on Porapak Q.

A method of determining benzene and trace amounts of 1,2-dibromoethane and 1,2-dichloroethane simultaneously in town air contaminated with motor-car exhaust gases (Stockholm) or in garage atmospheres has been described[73]. It is stressed that the sorption capacity of Porapak towards these compounds is greater than that of Tenax or Chromosorb-105.

The content of Halothane (2-chloro-2-bromo-1,1,1-trifluoroethane), an anaesthetic compound present in the air of surgical buildings at the 0.01 ppm level, has been measured[74] by preliminary concentration on Porapak Q and P.

The volatile flavouring agents in brewery products have been concentrated[75] by passing the distillate obtained from beer through an Amberlite column at 25 °C. Other workers[76] used XAD-2 to extract phenols and other compounds which interfere with the chromatographic separation of nucleotides from plant extracts (potato tubers, tomatoes, nuts). The conditions which favour the sorption of phenols on XAD-2 while suppressing the sorption of nucleotides, and those which give preferential sorption of nucleotides, were investigated. An attempt was made to correlate the electronic structure of the nucleotides with their affinity for XAD.

XAD-2 Amberlite has been used also to extract steroids from bile[77], urine[78,79], and milk[80], and morphine[81] and hexachlorophene compounds[82] from urine.

Spheron SE has been used for concentrating aromatic hydrocarbons, phenols, and pesticides from river waters of northern Bohemia[83].

Table 2. Determination of the trace impurities of organic compounds using porous polymer sorbents.

No.	Compound to be determined	Sorbent	Concentration conditions	Conditions and method of extraction	Chromatographic separation conditions	c_{min}	References
1	Amines (b.p. up to 300 °C) from air	Tenax	Glass column, 15 cm × 0.5 cm, air flow rate 1.3 litre h^{-1}	thermo-desorption at 250 °C	glass column, 2 m × 2 mm, filled with 8% Silar 10C on Chromosorb WHP, flame ionisation detector	1 ppb	[28]
2	Aromatic hydrocarbons, alcohols, chlorinated compounds, ketones from town or country air	Tenax	110 mm × 8 mm column, sample volume 3–30 litre, flow rate 100–300 ml min^{-1}	thermo-desorption	capillary column, flame ionisation or electron capture detector	–	[66]
3	Alkanes up to C_{18}, unsaturated and aromatic hydrocarbons, alcohols and ketones in industrial atmospheres	Tenax, Carbopak B	9 cm column with 0.28 g of Tenax and 0.45 g of Carbopak B, flow rate 30 ml min^{-1}	thermo-desorption	combined chromatograph and mass spectrometer	1 ppb	[52]
4	Ethylene from air	Porapak S	copper tube 10 cm × 6 mm containing 0.4 g of sorbent and cooled to −95 °C	concentrator heated rapidly to 100 °C and immersed in boiling water	3 m column filled with Porapak R, 40 °C, flame ionisation detector	0.01–0.1 ppb	[26]
5	Trichlorofluoromethane, chloroform, CCl_4, trichloroethylene, perchloroethylene from air	Porapak N	10 cm × 5 mm stainless steel column, sample volume 0.3–3 litre, flow rate 30–150 ml min^{-1}	thermo-desorption at 200 °C for 15 min	2 m column filled with 20% DC-200 on WAWDMCS Chromosorb, programmed temperature (from −40 to 140 °C, 16 K min^{-1}), electron capture detector	30–130 ppt	[71]
6	1,2-Dibromoethane, 1,2-dichloroethane, benzene from town air	Porapak Q, Chromosorb 105, Tenax	200 mm × 1.8 mm column, sample volume 3 litre, flow rate 50–100 ml min^{-1}	thermo-desorption at 175 °C, 3 min	2 m × 1.8 mm column filled with 6% poly-(*m*-phenyl ether) on Tenax	10–200 ppb	[73]
7	Carbonyl sulphide, CS_2, thiophene, tetrahydrothiophene from natural gas domestic supply	Porapak Q	31 cm × 4 mm column cooled in liquid O_2, sample volume 0.05–0.1 litre	heating from −183 to 100 °C, thermo-desorption at 100 °C	3 m × 3 mm column with Porapak Q 140 °C, flame photometer detector	0.7 ppm	[72]
8	Hydrocarbons, polynuclear aromatic compounds, dibenzofuran, etc., from mains water	XAD-2, –4, –7, –8, and mixtures	40 mm column, flow rate 80 ml min^{-1}	elution with acetone–methylene chloride mixture	analysis on SE-30, SP-2100, or Carbowax 20 M, flame-ionisation detector	1 ng $litre^{-1}$	[22]
9	Fenitrothion from water	XAD-2	10 cm column, sample volume 1 litre	elution with diethyl ether or acetone	column filled with 3% OV-101 on Cromosorb W, 190 °C	50 ppb	[51]
10	Acid food dyes from water	XAD-2	30 cm × 0.5 cm column	elution with methanol	analysis by the TLC method on XAD-2 plates	100 ng ml^{-1}	[86]
11	Fenitrothion and its decomposition products in water from areas treated with insecticides	XAD-2	10 cm × 1.9 cm column, sample volume 1 litre, flow rate 50 ml min^{-1}	elution with ethyl acetate	1.8 m × 4 mm column filled with 4% OV-101 and 6% OV-210 on Chromosorb WAW	10–30 ppb	[88]
12	Carbamate insecticides from water	XAD-2	35 cm × 1.5 cm column, sample volume 1 litre, flow rate 20 ml min^{-1}	elution with ethyl acetate	75 cm × 4 mm column with 3% Carbowax 20 M on Chromosorb WHP	0.01–1 ppm	[101]
13	Pesticides from river water	XAD-2	60 g of sorbent added to 20 litre of water and stirred for 8 h	sorbent stirred with 200 ml of toluene and ethylacetate (1 : 3) for 10 h	analysis by gas chromatography	0.3 ng $litre^{-1}$	[102]
14	Fenitrothion from water	XAD-4	30 cm × 1.9 cm column, sample volume 1 litre	elution with a solvent	analysis by TLC	50 μg $litre^{-1}$	[89]
15	Alcohols, ethers, ketones, aldehydes, alkylbenzenes, phenols, etc. in drinking water and in effluents	XAD-4	25 mm × 1.2–1.8 mm column, sample volume 50–100 μlitre, flow rate 0.8–1.2 ml min^{-1}	elution with 100 μlitre of acetone or acetone–CS_2 mixture	1.8 cm × 3 mm Tenax column	2–10 ppb	[92]
16	*p*-Nitrophenol-glucuronic acid from water	XAD-4	column with 10 g of sorbent flow rate 6 ml min^{-1}	elution with a water–acetone mixture (1 : 1)	analysis by TLC method	–	[103]
17	Fenitrothion and its decomposition products	XAD-7	flow rate 113 ml min^{-1}	elution with ethyl acetate	analysis by TLC method	50 ppb	[90]
18	Organo-chloro and organophosphorus pesticides	Tenax	48 cm × 1 cm column	elution with diethyl ether	gas-chromatographic analysis with electron capture detector	1 ppb	[85]
19	Toluene, *m*-cresol, phenol, pesticides in water	Spheron SE	40 mm × 5 mm column	elution with mixed solvents	120 cm × 3 mm column with Chromosorb-102, 200 °C	10–30 ppm	[83]

Table 2 (continued).

	Compound to be determined	Sorbent	Concentration conditions	Conditions and method of extraction	Chromatographic separation conditions	c_{min}	References
20	Phenol, *p*-nitrophenol, *p*-nitroaniline frow water	Styrene–divinyl-benzene–acrylonitrile	20 cm × 0.5 cm column flow rate 40 ml h^{-1}	elution with acetone	gas chromatographic analysis	—	[91]
21	Volatile metabolic products of micro-organisms	Tenax	–	thermo-desorption	2 m × 3 mm column with 5% Carbowax on Gas-chrome Z	–	[30]
22	Impurities from technical styrene monomer	Tenax	100 mm × 8 mm column	thermo-desorption at 290 °C for 15 min in a stream of helium, 20 ml min^{-1}	100 m × 0.5 mm capillary column, from 60 to 150 °C	–	[56]
23	Benzene and toluene from pentane	Tenax	100 mm × 1 mm column, cooled in water	thermo-desorption at 240 °C	50 m × 1 mm capillary column coated with PEG 20	10^{-5}–10^{-7} vol.%	[104]
24	Phenols from plant extracts	XAD-2	22.5 cm × 1.5 cm column	elution with methanol	–	–	[76]
25	Volatile flavouring agents from beer	XAD-2	60 mm × 7 mm column	elution with diethyl ether	2.8 m × 4 mm column with 10% Carbowax 20M on Chromosorb WAWDMCS, 50–200 °C, 3 K min^{-1}, flame ionisation or flame photometric detector	ppb–ppm	[75]
26	Volatile compounds from juices, wine, brandy, and biological fluids	Chromo-sorb-105	–	thermo-desorption	analysis on a capillary column	–	[70]

Notes. Two types of concentration unit have been recommended[105]: the mass of impurity in unit mass of sample (mass/mass) and the volume of impurity in unit volume of sample (volume/volume). Mass concentration units: 1×10^{-4} % ≡ 1 ppm, 1×10^{-7} % ≡ 1 ppb, and 1×10^{-10} % ≡ 1 ppt. Volume concentration units: 1×10^{-4} % ≡ 1 ppm, 1×10^{-7} % ≡ 1 ppb, 1×10^{-10} % ≡ 1 ppt. The choice of mass or volume units depends on the measurement method and on the practical use made of the results. Concentrations calculated from gas-chromatographic measurements have the dimensions of g ml^{-1}. They can be converted into ppm by using the formula[106] 1 ppm = 1 g $ml^{-1} \times 10^{-6}$ RT/pM, where R is the gas constant, cm^3 atm K^{-1} $mole^{-1}$, T is the temperature, K, p is the pressure, atm, and M is the molecular weight of the compound being analysed.

3. Extraction of Trace Impurities from Water

The use of polymer sorbents for concentrating trace amounts of organic compounds from water has been widely studied. A review paper[5] stresses the importance of a preliminary concentration, lists the requirements on the solvents used for extraction and on the water samples themselves, and discusses the properties and the applications of porous organic sorbents used for concentrating trace impurities.

In the same review[5] Dressler points out the similarity between the liquid extraction of organic impurities from water and the use of a solid sorbent: in both cases the dissolved impurities distribute themselves between the water and the extractant, whether a liquid solvent or a solid sorbent is used.

However, porous polymers offer a number of advantages over liquid extraction, since the adsorption of water on the polymer sorbent is negligibly small and the distribution coefficients of organic compounds in the polymer sorbent–water system tend towards infinity if the choice of sorbent has been optimised for the organic compound being extracted[5]. Sorbents with similar sorption properties can be used interchangeably in the concentrator. Dressler also notes[5] the superiority of Amberlites of the XAD series for concentrating traces of organic compounds from water (in particular, for the determination of biphenyls and poly-chlorobiphenyls in sea water, of chlorinated pesticides in drinking water, and of detergents, herbicides, insecticides, pesticides, hydrocarbons, and polyethoxy compounds in sewage).

The method of sampling the water and preparing the sample for analysis, and the process used for concentrating the impurities, depend on the concentration and on the chemical nature of the compounds in the water. Hydrocarbons (especially aromatic) are present in very small amounts in surface waters; effluents from the petrochemicals industry contain aromatic amines and phenols, and effluents from large-scale organic production plant contain pesticides and by-products of the paper, food, and pharmaceutical production industry. The permissible concentration of some organochloro pesticides in drinking water is 0.1 mg $litre^{-1}$, and a method of concentrating impurities is essential for effective analytical control.

Leoni and co-workers[84] have obtained up to 90% extraction of trace impurities (pesticides and polycyclic aromatic hydrocarbons) present in water at the 1 ppb level with Tenax. However, the capacity of the polymeric sorbents for given organic impurities depends on the other impurities present in water. In particular, mineral oils cause "deactivation" of Tenax[85], with a corresponding decrease in the percentage extraction of the trace impurities. The results obtained in the extraction of pesticides from water on Tenax were equivalent to those of the liquid extraction method in the case of drinking water and surface waters, especially when the sample was free from suspended matter which tend to adsorb some pesticides in large amounts. For waters containing suspended matter the results were equivalent only if the samples had been previously filtered[84]. The main advantages of the adsorption method (using Tenax GC) over liquid–liquid extraction are the long service life of the

sorbent, the ease of automation of the concentration process, and the avoidance of a solvent, which could complicate the subsequent analysis.

Most workers have used Amberlites of the XAD series to concentrate traces of organic compounds from water (see Table 1). The adsorbed impurities are usually extracted with organic solvents (Table 2).

Junk and co-workers[31] sorbed organic impurities from water on a 10 cm × 0.6 cm column filled with XAD-2 and XAD-4 (20–60 mesh) using the following concentration conditions: volume of sample 1000 ml, rate of flow of sample through the concentrator 30–50 ml min^{-1}. The sorbed compounds were extracted with diethyl ether, and the eluate was concentrated by evaporation and analysed by gas chromatography. The method was applied to a large number of model compounds present in water at the 10–100 ppb level (alcohols, aldehydes, ketones, esters, polynuclear aromatic compounds, pesticides, herbicides), and shown to give reasonably accurate and reproducible results. The conclusion was[31] that polymer sorbents are very effective for extracting neutral organic compounds from water. The sorbent was regenerated with methanol.

The use of Amberlite XAD-2 as a sorbent for extracting water-soluble acid dyes in the presence of triethylammonium bicarbonate has been recommended[86]. It is stressed that XAD-2 can selectively adsorb water-soluble organic compounds as a result of the interaction between the non-polar parts of the molecule and the hydrophobic sorbent surface. The use of XAD-2 for extracting polar compounds is limited by the low (or even negligible) affinity of these compounds for the sorbent.

The use of Amberlites of the XAD series (-1, -2, -4, -7, -8) for concentrating fulvic acid from aqueous solutions has been described[87]. The most effective concentration was achieved with Amberlites XAD-7 and -8, acrylate copolymers having an intermediate polarity and a high sorption capacity. The use of styrene–divinylbenzene copolymers (XAD-1, -2, -4) for concentrating fulvic acid is complicated by the slow adsorption of the acid molecule (diffusion-limited), and by the incomplete regeneration of the sorbent.

Amberlites of the XAD series (-2, -4, -7, -8) have been used also to extract impurities from mains water[22]. 13 Organic impurities were detected, including normal hydrocarbons, polynuclear aromatic compounds, and halogenated hydrocarbons. The most favourable sorption characteristics were obtained with a 1 : 1 mixture of XAD-4 and XAD-8.

Extensive studies have been devoted to the analysis of the organophosphorus insecticide Fenitrothion in spring waters. Some workers[51,88] used XAD-2 for this analysis, and showed that the sorbed insecticide is stable for a long time (up to 5 weeks) in a column filled with this sorbent. This is an important advantage of the adsorption method over the chloroform extraction method. Another useful feature of the method is the possibility of repeated regeneration (up to 20 times) of the sorption columns without loss of efficiency. The main disadvantage of the sorption method using XAD-2 is a fairly long analysis time (25–30 min). Increasing the flow rate of water through the adsorbent causes loss of the compounds being concentrated: the use of XAD-4 (which has a greater sorption capacity than XAD-2) is therefore recommended[89] for concentrating Fenitrothion, since it offers a shorter analysis time by allowing the flow rate of water through the adsorbent to be increased (1 lite of water in 2 min). Volpe and Mallet[90] extracted Fenitrothion and its decomposition products from water with XAD-7 Amberlite, which holds Fenitrothion more firmly than XAD-2 and XAD-4.

Ternary copolymers (styrene–divinylbenzene–acrylonitrile) have been used[91] for extracting phenolic compounds from water. The third component was found to improve the mechanical characteristics of the resin and its adsorption capacity for phenol, *p*-nitrophenol, and *p*-nitroaniline. The swelling of these copolymers in water and in acetone is very slight, and therefore the materials are convenient adsorbents for use under dynamic conditions.

As an alternative to the conventional columns for concentrating trace impurities of organic compounds from water, "mini-columns" containing ~80 mg of sorbents have been proposed[92,93]. Columns 25 mm long and 1.2–1.8 mm in diameter are filled with polymeric or hydrocarbon sorbents, the volume of sample is 50–100 μlitre, the adsorbed impurities (alcohols, esters, ketones, aldehydes, etc.) are extracted from the column with 50–100 μlitre of a suitable organic solvent, and 2 μlitre of the eluate are used in the subsequent gas-chromatographic analysis. This procedure avoids the need to evaporate the eluate to a smaller volume, and thus avoids the losses caused by the evaporation. The main shortcoming of the method is the very small size (~100 μlitre) of the water sample which seriously limits the sensitivity. tivity.

4. Use of Porous Polymer Sorbents Produced in the Soviet Union for Concentrating Trace Impurities

The porous polymer sorbents made in the Soviet Union which have been used for concentrating traces of organic compounds include Polisorb-1, Polisorbimid-1, and a sorbent based on polyphenylquinoxaline.

Polisorb-1 is a porous copolymer of styrene and divinylbenzene[94], similar in chemical nature and in structure to sorbents of the Amberlite (in particular, XAD-2) and Chromosorb-102 type. It can be used as an alternative to these sorbents after appropriate pre-treatment[5].

Polisorbimid-1, a polycondensation product of pyromellitic dianhydride and diaminodiphenyl ether, is a thermally stable polymer sorbent (up to 400–450 °C).[94,95] Polisorbimid-1 has been found[96] to retain polar compounds and aromatic hydrocarbons significantly better than Tenax. This sorbent has been used successfully for concentrating traces of oxygen-containing impurities and aromatic hydrocarbons from air. The concentrated impurities were desorbed at 280 °C in a stream of carrier gas, and they were separated and identified gas-chromatographically with a mass spectrometer detector[96].

The sorbent based on polyphenylquinoxaline (PFKh) proposed[97] for the separation and concentration of volatile organic compounds is also thermally stable: its maximum working temperature is 280–300 °C. The gas-chromatographic properties of this sorbent are described in Refs. 98 and 99. The PFKh is pre-conditioned in the concentrator column in a stream of carrier gas by raising its temperature from 100 to 280 °C (in steps of ~50 K) and holding it for 2–3 h at each temperature.

The possibility of using PFKh for concentrating traces of organic compounds from air has been studied in detail[100], and the retention volume was found to be greater than on Tenax for a large number of organic compounds (vinyl chloride, hexene, hept-1-ene, benzene, toluene, ethylbenzene, cumene, pseudocumene, cyclohexanone, and mesitylene) in the effluents from the production and utilisation of structural polymers based on poly(vinyl chloride). For example, at 20 °C the specific retention volume for vinyl chloride on Tenax is 270 ml, as compared with 2250 ml on PFKh. This allows large quantities of the components to be accumulated in the concentrator before break-through, thus increasing the precision of the determination of trace impurities. The impurities are desorbed at 200–280 °C, depending on their chemical nature.

The increasing penetration of these polymer sorbents into analytical practice should hasten the solution of many important problems in the protection of the environment from contamination by toxic trace impurities.

Examples of the determination of traces of organic compounds in gaseous and in liquid media by using porous polymer r sorbents are given in Table 2. The Table also states the conditions used for the concentration, desorption, and gas-chromatographic analysis of the impurities.

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This review of published work shows that porous polymer sorbents are now widely used for concentrating trace impurities of organic compounds in gaseous or in liquid media. Their success is due to the great variety of chemical forms and structural characteristics offered by these materials, which allow the choice of the most suitable sorbent for concentrating any given impurity. Another important advantage of polymer sorbents is the associated use of thermo-desorption techniques, which simplify the concentration process and make its automation easier. Polymeric sorbents can be used repeatedly without loss of adsorption efficiency. The continuing expansion of the range of these sorbents, and the penetration of new sorbents into the analytical practice, should result in an increased sensitivity for the determination of trace impurities as well as widening the range of compounds which can be detected.

The use of porous polymer sorbents for concentrating trace impurities will extend the boundaries of gas chromatography as applied to the control of toxic substances in the environment—an essential stage in the fight against the pollution of the atmosphere and hydrosphere of our plant.

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Correlation Functions of One-dimensional Systems

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The calculation of correlation functions describing the structure in space of one-dimensional systems is discussed, and various approaches to this problem are analysed. Examples of the use of correlation functions to interpret experimental X-ray and neutron scattering data and to calculate transition temperatures in quasi-one-dimensional systems are given.
The bibliography includes 41 references.

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I. INTRODUCTION

In the light of recent advances in the synthesis of interesting quasi-one-dimensional compounds such as electrically conducting donor–acceptor complexes based on tetracyanoquinonedimethane (TCNQ),[1] polyacetylene doped with donors or acceptors[2], etc. the practical importance of one-dimensional physics is now self-evident. We know that one-dimensional system have a number of special attributes which produce a striking difference between one-dimensional and three-dimensional systems. In particular, and in spite of the relative simplicity of the one-dimensional systems, the well tried approximations used in the solution of three-dimensional problems are not always applicable to one-dimensional problems, and advances in one-dimensional physics must await the development of new methods.

Though theoretical studies of one-dimensional quantum systems began before the last war, detailed and organised work only began in the 1960's under the stimulus of successes in the preparation of these materials. During this period, which extends over 10–15 years, theoretical efforts were aimed mainly at the development of methods of calculating the energy characteristics (ground state energy, excitation spectra, etc.) and the thermodynamic parameters of one-dimensional systems. Approximate methods of calculating energies (by the specific variational method) were obtained, and allowed the energy of one-dimensional systems to be calculated very accurately[3]. Furthermore, for some one-dimensional models accurate results were obtained by a method which follows from the work of Bethe[3]. Numerical studies of systems consisting of a finite number of particles have also been very useful[4].

The main outcome of all this work was a realisation of the importance and of the specific features of correlation effects in one-dimensional systems, and the development of accurate methods of allowing for these effects. In spite of the continuing uncertainties in our understanding of some aspects of the energy characteristics (for example, the accurate correction for electron–phonon interactions, and in particular

† This and the following reviews are based on plenary papers presented to the Twelfth All-Union Congress on Organic Semiconductors (October 1982).

for the Peierls transition[5]), the energy problem can be considered (on the whole) to have been solved, and the main focus of attention is now a problem of a different kind: the calculation of the correlation functions of one-dimensional systems.

The correlation functions are different types of average over the wave functions of the system, which characterise its spatial structure as well as determining its response to various external stimuli (in particular, the diffraction of X-rays or neutrons by the system). The information contained in the correlation function is much more profuse than that implicit in a knowledge of the energy spectrum or of the thermodynamics of the system. As an example, we note that the most accurate calculations of the extent of charge transfer in quasi-one-dimensional donor–acceptor crystals of the TTF–TCNQ type (where TTF is tetrathiofulvalene) were based on diffuse X-ray and neutron diffraction spectra[6,7]. However, we should stress that the calculation of correlation functions is a much more complex problem than the calculation of energies. This is mainly because the former requires a knowledge of the wave functions of the system, and whereas the variational method gives acceptable results in calculations of energy it is far from satisfactory when applied to the calculation of wave functions. The method of Bethe, mentioned above, also gives accurate values of the energy but is unacceptable as a method of calculating wave functions. These difficulties are responsible for the lack (until recently) of serious attempts to calculate the correlation functions of one-dimensional systems, although accurate results were obtained[8,9] for a few, isolated model systems. The work done in the first stage has been expertly reviewed (see, for example, Ref.10), and is fully understood by theoreticians as well as by experimental scientists; on the other hand the problem of calculating correlation functions, which has been actively investigated only during the past 6–8 years, is still far from being solved, and has not yet been reviewed in detail. The various approaches to the solution of this problem are based on hypotheses which are difficult to prove and not always well founded, and therefore the acceptance of results from various laboratories is not universal. The aim of this paper is to review recent progress in this field and to discuss the results obtained so far.

II. CORRELATION FUNCTIONS OF THE CONTINUUM MODEL OF A FERMI GAS

We shall examine most closely two specific correlators (or correlation functions): the one-particle density matrix $\rho(R)$, defined by the integral

$$\rho(R) = \rho \int \Psi^*(R, x_2, \ldots x_N)\, \Psi(0, x_2, \ldots, x_N)\, \mathrm{d}x_2 \ldots \mathrm{d}x_N$$

[where $\Psi(x_1, \ldots, x_N)$ is the wave function of the system, depending on the coordinates of the particles $(x_1, \ldots, x_N)$], and the pair correlation function $G(R, t)$,

$$G(R, t) = \langle \rho(0, 0)\, \rho(R, t) \rangle$$

where $\rho(R, t)$ is a density operator depending on the time t, and the angle brackets denote statistical averaging. The function $G(R, t)$ defines the probability of finding any particle of the system at a distance R from the given particle at time t. In particular, for $t = 0$ and zero temperature ($T = 0$) we can write

$$G(R, 0) = \rho^2 \int \Psi^*(0, R, x_3, \ldots, x_N)\, \Psi(0, R, x_3, \ldots, x_N)\, \mathrm{d}x_3 \ldots \mathrm{d}x_N .$$

The correlator $\rho(R)$ is interesting because its Fourier transform $n(k)$ is a function of the distribution of the particles in momentum k at $T = 0$. Also important is the Fourier transform of the correlator $G(R, t)$ (the dynamic form-factor $S(k, \omega)$, where ω is the frequency[11]), which determines the probability of scattering of neutrons and X-rays. We shall be mainly interested in the values of these correlators for large distances and long times.

The most characteristic feature of one-dimensional systems is the lack of long-range order even at $T = 0$, with a few exceptions, which will be mentioned below. This means that the value of the correlators is an inverse function of distance. The determination of this function is one of the theoretical problems facing us. In other words, we have the asymptotic laws $\rho(R) \propto R^{-\kappa}$ and $G(R, 0) \propto R^{-\alpha}$, and we are required to find κ and α (which are sometimes called the critical indices).

It could be useful to dwell briefly on one aspect of the lack of long-range order in one-dimensional systems: the one-dimensional superconductor problem. It is often stated in the literature that one-dimensional superconductivity is impossible owing to the lack of long-range order. These statements rely on the analogy with a Bose gas, in which super-fluidity occurs as a result of a phase transition in the Bose condensate state whose matrix (or, more accurately, the non-diagonal elements of whose matrix) do not vanish for $R \to \infty$. We should stress that there is as yet no strict proof that one dimensional superconductivity is impossible in the absence of long-range order, and furthermore that metastable states with a non-zero current can exist in one-dimensional systems. Though phase transitions at $T \neq 0$ are impossible in one-dimensional systems, and these metastable states do not contribute long-range order, their life-times can be very long because states with a non-zero current and states with a zero current are separated by high activation barriers, and the probability of transitions between the two states is calculated[12] to be very small.

Two main approaches to the calculation of correlation functions are available at present. It has been assumed[13] that the behaviour of the correlation functions of one-dimensional Fermi systems (with which we shall be concerned in this review) at large distances is determined by gap-free long-wave excitations of the acoustic type (which are in fact responsible for the breakdown of long-range order). By allowing for these excitations and ignoring all the others we can obtain explicit expressions for the correlation functions.

The other approach to the calculation of correlators relies on the linearisation of the quadratic Fermion spectrum, i.e. on the replacement of $k^2/2m$ by $v_F k$ (where m is the mass of the Fermion and v_F is the Fermi velocity) and on the definition of two kinds of particle with $k = k_F$ and $k = -k_F$ respectively (where k_F is the Fermi momentum, related to the particle density ρ by the expression $k_F = \pi\rho$). Within the limitations of the "linear model" thus obtained, accurate calculations are possible[14–16].

The correlation functions obtained by these two approaches are qualitatively consistent. Their most characteristic features are the power-law decrease at large distances and the smooth variation of the critical indices with the corresponding electron–electron interaction constant. When evaluating the two approaches we should remember that the hypothesis of the dominant role of acoustic excitations has not been strictly justified. Furthermore, as we shall show below, the asymptotic behaviour of the pair correlation function can be inferred from the properties of the structure factor $S(k)$ at $k = 2k_F$, $4k_F$, etc., and therefore it cannot be associated with excitations of the acoustic type. On the other hand, the approach based on the linearisation of the quadratic Fermion spectrum

also has some weaknesses, the most serious of which is the inadequate symmetry of the complete wave function of the system (due to the introduction of two kinds of particle), which cannot be justified (say) by the expansion of various physical quantities in a power series of a small interaction constant.

Thus both approaches rely on plausible but not strictly justified assumptions. In our calculation[17] of the correlation functions we have developed a variant of perturbation theory which uses a non-interacting Fermi gas as the zeroth approximation, and therefore allows standard corrections to be applied to the correlation function. Our method treats a one-dimensional system of N particles (whose spin is ignored to simplify the problem), distributed over the region $[0, L]$, by the continuum model of a Fermi gas, whose Hamiltonian is

$$\hat{H} = -\sum_{i=1}^{N} \frac{\partial^2}{\partial x_i^2} + g \sum_{i \neq j}^{N} V(x_i - x_j) . \qquad (1)$$

Here $V(x)$ is the interaction potential, assumed to be arbitrary, and g is the interaction constant. As stated above, the most serious difficulty in the calculation of the correlators is our lack of knowledge of the form of the wave functions of this system. We started from the following representation of the wave function of the ground state:

$$\Psi(x_1, \ldots, x_N) = \Psi_0(x_1, \ldots, x_N) \cdot \exp[\Phi(x_1, \ldots, x_N)] \qquad (2)$$

where Ψ_0 is the wave function of the system without interaction (the Slater determinant), which is antisymmetrical with respect to permutation of particle coordinates, and $\Phi(x_1, \ldots, x_N)$ is a symmetric function.

Inserting Ψ into the Schrödinger equation gives an equation for Φ. Since the function Φ is symmetric, the equation obtained is the Hamiltonian of the Bose particles. This "Bosonisation" of the Fermi problem has several interesting consquences, which lack of space prevents us from discussing. It is found that Φ takes the form

$$\Phi = \sum_{i,j} \Phi_2(x_i - x_j) + \sum_{i,j,l} \Phi_3(x_i - x_j, x_j - x_l) + \ldots \qquad (3)$$

i.e. it is made up of functions for two, three, etc. particles. It is also found (even more importantly) that the two-particle function $\Phi_2(x)$ plays the main role in determining the correlation properties. Furthermore, the asymptote of the correlators at large distances is given by the asymptote of the Fourier transform of $\Phi_2(x)$: the function $\sigma_2(k)$ for $k \to 0$.

Thus we have shown that detailed information on the wave function is not essential to the determination of the most important correlation properties of the system, and we have reduced the problem of obtaining the correlators to finding the asymptote of the function $\sigma_2(k)$, followed by suitable averaging. Though each of these problems is fairly difficult, they are much simpler than the initial problem. Our calculations show[18] that the asymptotic form of the function $\sigma_2(k)$ for $k \to 0$ is

$$\sigma_2(k) = \pi(c_0 - c)/2c_0|k| \qquad (4)$$

where c and c_0 are the velocities of sound in the system having interaction and in the system having $V(x) = 0$ respectively. We note that the velocity of sound appears in the expression for the excitation energy: $\varepsilon(k) = c|k|$ for $k \to 0$. The velocity of sound determined in this way is consistent with the value obtained by thermodynamic arguments.

Now let us consider the density matrix $\rho(R)$. In order to evaluate it we developed a special graphical method[17] from which the asymptotic form of the $\rho(R)$ dependence at large distances R can be obtained:

$$\rho(R) = \sin(k_F R)/(\pi R k_F)^{\varkappa}; \quad \varkappa = (c_0^2 + c^2)/2cc_0 . \qquad (5)$$

Since $c = c(g)$, the critical index κ varies continuously as a function of g. This behaviour of κ is typical of one-dimensional quantum systems. As was stated above, the Fourier transform of $\rho(R)$, i.e. the function $n(k)$, is a function of the distribution of the particles in momentum. The most interesting property of the function $n(k)$ is the absence of a discontinuity at $k = k_F$:

$$n(k) = \frac{1}{2}\{1 + \operatorname{sign}(k_F - k)\,|k - k_F|^{\varkappa - 1}\}; \quad \varkappa - 1 = (c - c_0)^2/2cc_0 . \qquad (6)$$

The jump in the momentum distribution of the particles is absent even when the g value is so small that the one-dimensional system behaves very differently from a three-dimensional system. It has been shown[19,20] that in the three-dimensional case the jump persists for $g \neq 0$, though it is no longer equal to 1.

Qualitatively similar results were obtained by the linear model[8]. However, we should note that in the linear model the critical index κ has a different value, and that for some types of interaction potential (in particular, in the case of a δ-function potential) the linear model gives an incorrect value of κ even for $g \to 0$.

We may now consider the other correlator: the pair correlation function $G(R, t)$ and its Fourier transform [the function $S(k, \omega)$]. This correlator is most conveniently discussed by starting with a special case: strong repulsion between the electrons. In this case the correlator of interest to us can be calculated exactly: thus the results can be compared with those of the linear model, and furthermore the form of the pair correlation function can be determined for arbitrary values of the interaction constant.

Let us examine a system defined by the Hamiltonian (1). The potential $V(x)$ which appears in it can be, for example, a power function, or it can have the form $V(x) = \exp(-\gamma|x|)$, where γ^{-1} is the interaction radius. An exact analysis of this system for $g \to \infty$ and low enough temperatures is possible because of the well-known formation of a Wigner crystal with a lattice constant $a = 1/\rho = L/N$.[18] Introducing the new variable

$$x_n = na + \xi_n$$

and truncating the expansion of the potential energy at the term quadratic in ξ_n we obtain the Hamiltonian for a system of harmonic oscillators with long-range effects, which can be reduced in the normal way to the Hamiltonian for a system of non-interacting phonons.

The spectrum of these oscillators defines the energy of the elementary excitations of the Fermi gas. These excitations (Fig. 1) are of the acoustic type at low values of the momentum ($q \to 0$):

$$\omega(q) = c|q|; \quad c = a\left(2g \sum_{n=1}^{\infty} V''(na)\, n^2\right)^{1/2} \qquad (7)$$

and are periodic, with a periodicity of $2k_F$, which is characteristic of one-dimensional systems in general.

In this limit ($g \to \infty$) the wave functions of the initial system reduce to the standard oscillator functions, and the calculation of $G(R, t)$ involves only taking the Gaussian integrals. The expression for $G(R, t)$ is quite cumbersome[18], and will not be reproduced here. We shall examine some

special cases only. For $t = 0$ and $r = 0$ the function $h(R) = G(R, 0) - \rho^2$ becomes

$$h(R) = 2\rho^2 \sum_{s=1}^{\infty} \cos(2k_F sR)\,(R\rho)^{-2\mu s^2};\ \mu = 2k_F/c \quad (8)$$

The asymptotic behaviour of this correlator for $R \to \infty$ is determined by the first term of this sum (for $s = 1$):

$$h(R) = 2\rho^2 \cos(2k_F R) \cdot (R\rho)^{-2\mu} \quad (9)$$

i.e. the critical index is $\alpha = 4k_F/c$. We note from formula (9) that at $T = 0$ the function $h(R)$ decreases with distance by a power law whose index depends on g. For $T \neq 0$ the function $h(R)$ decays exponentially with a correlation radius $\propto T^{-1}$.

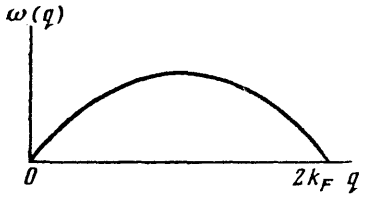


Figure 1. Spectrum of the elementary excitations in a one-dimensional Fermi gas.

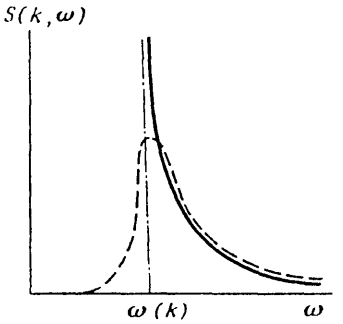


Figure 2. Plots of $S(k, \omega)$ against ω for a fixed k. The full line is for $T = 0$, the broken line for $T \neq 0$.

The following remarks are relevant in connection with the formula for $h(R)$. As stated above, the correlator $h(R)$ has been calculated exactly for some special forms of the potential $V(x)$ and some special values of g (in particular, for the $V(x) = x^{-2}$ potential, used in the Sutherland model[21-24]). The velocity of sound c is also known for these special cases. By inserting these values of c into formula (9) for $h(R)$ we obtain good agreement with all the known exact values. Furthermore, $h(R)$ can be calculated in the limit of small g by the method which we used to calculate the density matrix: comparison of the results[19] shows that the formula for $h(R)$ is valid in this case also. These observations suggest that the expression for $h(R)$ can be used for all $g > 0$ and $T = 0$ if an exact value of the velocity of sound is available for the parameter c which appears in the expression.

Thus the asymptotic behaviour of both $h(R)$ and $\rho(R)$ is known if the velocity of sound c is known. The problem of calculating c is much simpler than the calculation of the correlator, since c is effectively one of the energy parameters of the system, which can be calculated by well tried approximations. For some of the models the c value is accurately known. As g varies from 0 to ∞ the parameter α varies from 2 to 0. It is interesting to compare the expression for $h(R)$ with the corresponding expression of the linear model. The latter also gives a power-law decrease in the correlator as $R \to \infty$, but with a different exponent, except at low values of g.

The Fourier transform of $G(R, t)$—the dynamic structure factor $S(k, \omega)$—defines the probability of scattering neutrons and X-rays. The plot of $S(k, \omega)$ against ω (Fig.2) for a fixed value of k shows a singularity at $\omega \to \omega(k)$ for all $g > 0$ and fixed k ($S(k, \omega)_{g=0} = \text{const.}$), described by a power law with the exponent $1 - \alpha/2$. For $T \neq 0$ this singularity is smoothed out, and a maximum appears in $S(k, \omega)$ at $\omega = \omega(k)$ (broken line in Fig.2).

It is interesting also to consider the correlator $S(k)$, i.e. the static structure factor which determines the probability of elastic scattering of X-rays and is the Fourier transform of the correlator $h(R)$.

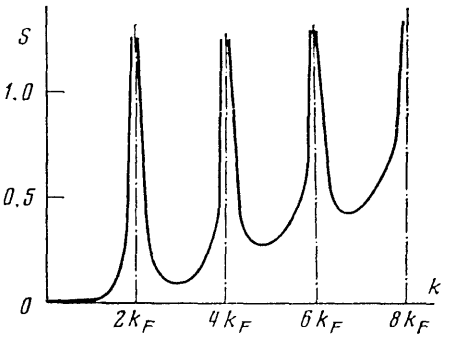


Figure 3. $S(k)$ dependence in the Sutherland model for $g = 2 \times 10^4$ and $T = 0$.[18]

Figs.3 and 4 show plots of the function $S(k)$ at $T = 0$ and at $T \neq 0$ for different values of g in the Sutherland model. At $T = 0$ the function $S(k)$ is discontinuous at the k values $k \to 2k_F n$, and we can write $S(k) = |k - 2k_F n|^{\alpha n^2 - 1}$. The number of peaks, i.e. the number of points n at which the function diverges, satisfies the condition $c > 4k_F n^2$, and therefore the number of peaks increases with g. We also note that the leading term of the asymptote of the function $h(R)$ is determined by the singularity in $S(k)$ at $k = 2k_F$. The effects at $k = \pm 4k_F$, $\pm 6k_F$, etc. correspond to the further terms of the expansion ($s = 2$, 3, etc.) in formula (8). We should note that the singularities of the function $S(k)$ at $k = \pm 2k_F n$ (with $n \geq 2$) are "lost" in the linear model. At $T \neq 0$ the discontinuities in the function $S(k)$ are rounded off, and the value of $S(k)$ is finite for all k, with

$$S(0) = 2k_B T/c^2;\quad S(2k_F n) = \coth(2\pi^2 n^2 k_B T/c^2) \quad (10)$$

As the temperature is raised the height of the peaks decreases. It can be shown that the function $S(k)$ plotted in Fig.4 is valid not only at low temperatures (to which our

discussion applies) but even in the high temperature limit, where the classical approximation can be used. It was found[25,26] that the function $S(k)$ has maxima at $k = 2k_F n$, and the height of the peaks decreases as n increases. These calculations were intended to explain experimental data[26] on the diffuse scattering of X-rays by linear chains of mercury atoms in the quasi-one-dimensional $Hg_{3-\delta}AsF_6$ system. The $S(k)$ dependence obtained experimentally is similar to that shown in Fig.4 and agrees well with the calculations[25,26]. It follows from the expressions for $h(R)$ and $S(k)$ that an interacting Fermi gas is structurally closer to a one-dimensional solid than to a liquid.

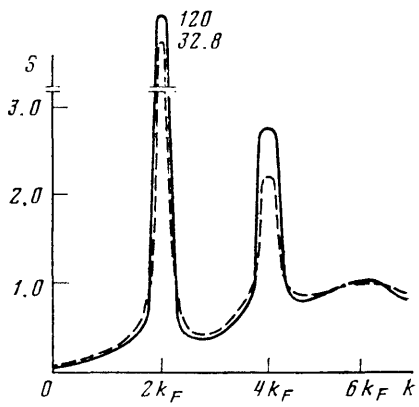


Figure 4. $S(k)$ dependence in the Sutherland model for $g = 200$. Full line $k_B T/\rho^2 = 3/5$; broken line $k_B T/\rho^2 = 3$. The numbers on the curves denote the height of the peak at $k = 2k_F$.[18]

The main conclusions from the above discussion of the correlators for a one-dimensional interacting Fermi gas can be formulated as follows. At large distances and $T = 0$ the correlation functions decrease by a power law, with an exponent expressed simply in terms of the velocity of sound. Reliable methods of calculating the velocity of sound are available, and for some models this parameter is already accurately known. Both methods of calculating the correlators (by linearising the problem or by postulating predominantly acoustic excitation in the formulation of the special features of the correlators) give functionally correct predictions of the asymptotes of the correlators, but the critical exponents are correctly calculated only for small g: evidently, the linearisation procedure as described is valid only in this region of g values.

A new approach to the calculation of correlators has been proposed recently by Haldane[27], who used assumptions basically similar to those of Ref.13 to convert the problem into an oscillator problem and obtained experessions for the correlators identical to ours.

III. LATTICE FERMI GAS

So far our discussion has been confined to the continuum model of a one-dimensional Fermi gas. A more realistic model of the system is provided by the lattice Fermi gas, which describes a system of N interacting electrons located at M centres, with $N \to \infty$ and $M \to \infty$ and $N/M = \rho$. The continuum and the lattice model have a great deal in common both from the electronic structure and from the correlator point of view. Thus, the correlator $\rho(R)$ for the lattice Fermi gas can be calculated as in the continuum case, the steps in the Fermi distribution becomes diffuse[28] however weak the interaction, with a critical index κ for $g \ll 1$ given by

$$\varkappa = 1 + g^2 v^2(0)/32\pi^2\beta^2 \sin^2(\pi\rho/2)$$

where $v(q)$ is the Fourier transform of the function $V(x)$ [$v(0) = v(q = 0)$, and β is the resonance integral].

At the same time, lattice systems offer a number of special features. For example, in contrast to continuum models (for which the elementary excitation spectrum has no gap) the lattice systems can have a gap. Lastly, for stated values of the parameters the lattice systems allow long-range order at $T = 0$.

Let us consider the simplest (but by no means trivial) lattice model: a Fermi gas without spins and with interactions between nearest neighbours. Its Hamiltonian is

$$\hat{H} = -\beta \sum_{n=1}^{N} (a_n^+ a_{n+1} + a_{n+1}^+ a_n) + g \sum_{n=1}^{N} a_n^+ a_n a_{n+1}^+ a_{n+1}; \; \rho = 1/2; \; g > 0 \quad (11)$$

where a_n^+ and a_n are operators for the generation and annihilation of Fermions on the nth centre. This system is interesting also because it is equivalent to the anisotropic antiferromagnetic Heisenberg model. Mathematically, the term "equivalent" postulates the existence of a canonical transformation[29] which converts the Fermi operators into spin operators, so that Eqn.(11) reduces to the Hamiltonian of the Heisenberg model.

An interesting property of this system is the presence of a gap in the elementary excitation spectrum for $g > 2\beta$.[30,31] In this range of g values the system displays long-range order, i.e. the correlator $h(R)$ tends towards a finite limit determined by the ratio g/β at $R \to \infty$. In magnetic systems this implies the existence of non-zero magnetisation of the sublattices. The asymptote of $h(R)$ differs from its limiting value, first calculated by Baxter[32], by an exponentially small quantity. For $g < 2\beta$ the spectrum of the system no longer has a gap, and the long-range order disappears[30,31]. If controlled changes in β (say) are imposed on the system a metal $\to$ dielectric transition is obtained at $\beta = g/2$, when both the gap and the long-range order disappear.

Unfortunately, no strict calculations of pair correlation functions in a metallic phase have been reported yet, and only approximate expressions for this correlatore are so far available. They were obtained[33–35] from the following considerations. The spectrum of elementary excitations of the system is of the form shown in Fig.5.[36] The cross-hatched region is called the two-parameter continuum; its upper and lower limits are the $\varepsilon_2(k)$ and $\varepsilon_1(k)$ curves, given (for $g = 2\beta$, for example) by the expressions

$$\varepsilon_2(k) = \pi g |\sin(k/2)|; \; \varepsilon_1(k) = (\pi g/2)|\sin k|.$$

Against each triangle in Fig.5 is shown the value of $S(k, \omega)$ for the corresponding k and ω obtained[33] in calculations for systems with a finite number of electrons $N = 10$. These calculations show that for the states lying above the two-parameter continuum the $S(k, \omega)$ values are at least an order of magnitude smaller than for the states within the continuum. Assuming that even at $N \to \infty$ the higher states do not contribute significantly, the following expression for $S(k, \omega)$

was obtained[33]

$$S(k,\ \omega) = A\theta[\omega - \varepsilon_1(k)]\,\theta[\varepsilon_2(k) - \omega]\cdot[\omega^2 - \varepsilon_1^2(k)]^{-\lambda_1}\,[\varepsilon_2^2(k) - \omega^2]^{-\lambda_2}$$

$$\theta(x) = \begin{cases} 1, & x > 1 \\ 0, & x \leqslant 0 \end{cases},$$

where A is a constant, and the exponents λ_1 and λ_2 are chosen in relation to known constraints (for example, for $g = 2\beta$, $\lambda_1 = 1/2$ and $\lambda_2 = 0$). The approximate expression for $S(k, \omega)$ thus obtained is functionally similar to the corresponding expression of the continuum model, confirming the similarity between the continuum and the lattice model in the metallic phase.

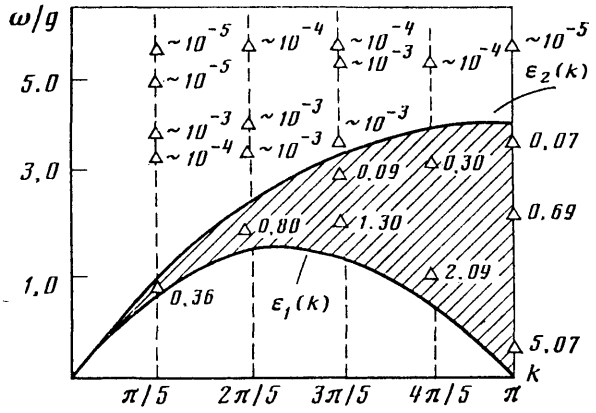


Figure 5. Excitation spectrum of a lattice Fermi gas and $S(k, \omega)$ values for $N = 10$.[33]

IV. EXAMPLES OF THE USE OF CORRELATION FUNCTIONS

We shall illustrate the above discussion by giving two examples of the use of correlation functions: 1) to interpret experimental data on the inelastic scattering of neutrons by a one-dimensional system, and 2) to calculate the critical phase transition temperatures in quasi-one-dimensional systems.

1) The most meaningful experiments on the inelastic scattering of neutrons by one-dimensional systems of the present type were carried out with the one-dimensional antiferromagnetic CPC $[CuCl_2.2N(C_5D_5)]$.[37,38] As was stated above, a one-dimensional antiferromagnetic is equivalent to a one-dimensional lattice Fermi gas with repulsions between particles. Experimental data on the inelastic neutron scattering cross-section of CPC are reproduced in Fig.6a. We note that the asymmetry of the line and the intensity at the maximum increase as the temperature is lowered. The asymmetry was initially thought[37] to be an apparatus effect, but its reality was confirmed by later experiments[38]. The effect is easily explained in terms of the temperature dependence of $S(k, \omega)$, theoretically predicted (see Fig.2) and arising from the properties of the function $S(k, \omega)$ at $\omega = \omega(k)$.

The integral scattering intensity experimentally observed at $T = 1.3$ K (Fig.6b) suggests a singularity in $S(k)$ at $k \to 2k_F$ (in this case $k_F = \pi/2$) and agrees very well with the theoretical expression given by Müller[33].

2) The calculation of the critical transition temperature in quasi-one-dimensional systems. As we have already stated, long-range order is absent in one-dimensional systems at $T \neq 0$ (though it can exist at $T = 0$ in the lattice systems discussed above). In real systems a small but significant lateral interaction between the one-dimensional systems (filaments) is always present. As a result, at low enough temperatures the one-dimensional systems becomes effectively three-dimensional, and they develop long-range order (which disappears at $T = T_{cr}$).

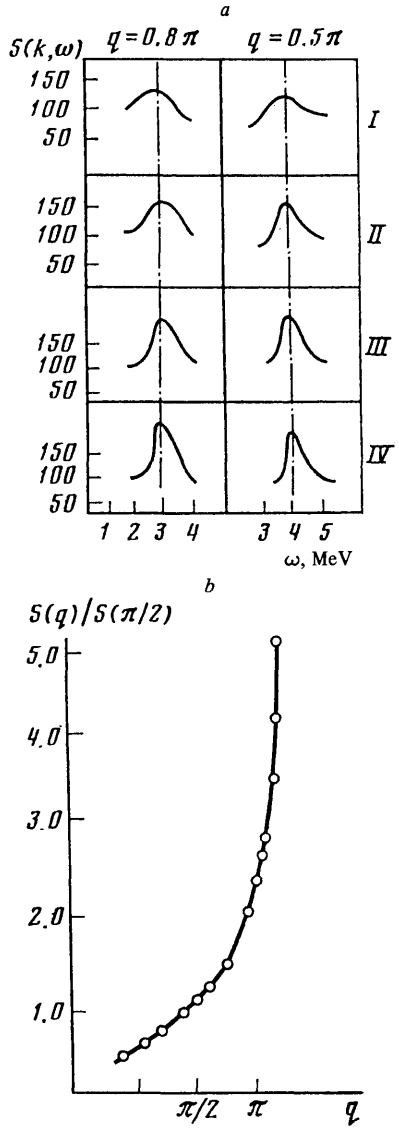


Figure 6. (*a*) Inelastic neutron scattering cross-section for CPC in relative units for two values of q, and (*b*) integral scattering intensity, for different temperatures (T): *I*) 8.0, *II*) 4.0, *III*) 2.0, *IV*) 1.3 K.[37,38]

We shall illustrate the calculation of T_{cr} from a knowledge of the one-dimensional correlators by considering the trivial but very revealing example[39] of a two-dimensional system of

ferromagnetic Eising chains with weak transverse interactions. The Hamiltonian of this system is

$$\hat{H} = -J_{\parallel} \sum_{i,m} S^z_{i,m} S^z_{i+1,m} - J_{\perp} \sum_{i,m} S^z_{i,m} S^z_{i,m+1};\ J_{\parallel} > 0;\ J_{\perp} > 0\ , \quad (12)$$

where $J_{\parallel}$ and $J_{\perp}$ are the exchange integrals for the interaction of nearest neighbours along chains and at right angles to the chains respectively, and $S^z_{i,m}$ is the operator for the z-component of the spin at the lattice point numbered (i, m).

We shall use the self-consistent field approximation and replace one of the operators in the second term by its average value $\langle S^z \rangle$:

$$\hat{H} = -J_{\parallel} \sum_{i,m} S^z_{i,m} S^z_{i+1,m} - 2J_{\perp} \langle S^z \rangle \sum_{i,m} S^z_{i,m}\ , \quad (13)$$

with the self-consistence condition

$$\langle S^z \rangle = \mathrm{Sp}\, S^z_{i,m} \exp(-\hat{H}/k_B T) / \mathrm{Sp} \exp(-\hat{H}/k_B T)\ . \quad (14)$$

At $T \to T_{cr}$ we have $\langle S^z \rangle \to 0$, and by expanding the right-hand side of (15) into a power series in $\langle S^z \rangle$ we obtain the following expression for calculating T_{cr}:

$$k_B T_{cr} = 2J_{\perp} \sum_n \langle S^z_0 S^z_n \rangle\ . \quad (15)$$

The one-dimensional correlation function $\langle S^z_0 S^z_n \rangle$ appears in this expression. Thus, knowing the one-dimensional correlator $\langle S^z_0 S^z_n \rangle = \tanh^n |(J_{\parallel}/4k_B T)/4$, we can calculate T_{cr} by solving Eqn.(15):

$$k_B T_{cr} = 2J_{\parallel} / \ln (J_{\parallel}/J_{\perp})\ .$$

The exact value of T_{cr}, obtained by solving Onsager's equation, is given by

$$k_B T_{cr} = 2J_{\parallel} / \ln (2J_{\parallel}/J_{\perp})\ .$$

These calculations can easily be generalised to include more complex systems[13,40,41]. For example, we can use exactly the same arguments to calculate T_{cr} for a three-dimensional lattice gas with weak transverse interactions[41]:

$$\hat{H} = \hat{H}_0 + \hat{H}_1;\ \hat{H}_0 = -\beta \sum_{i,m} (a^+_{i,m} a_{i+1,m} + a^+_{i+1,m} a_{i,m}) +$$
$$+ g_{\parallel} \sum_{i,m} a^+_{i,m} a_{i,m} a^+_{i+1,m} a_{i+1,m};\quad \hat{H}_1 = g_{\perp} \sum_{i,m} a^+_{i,m} a_{i,m} a^+_{i,m+1} a_{i,m+1}\ .$$

The subscript i gives the number of the site along the filament, whereas m defines the site in the perpendicular direction. For $T < T_{cr}$ we have a long-range order phase (called the phase with a charge density wave), in which three-dimensional effects appear, whereas for $T > T_{cr}$ the system is essentially one-dimensional.

Using the self-consistent field approximation and inserting the self-consistence condition we arrive at the equation

$$1 = 2v \int_0^{(k_B T_{cr})^{-1}} d\tau \sum_n (-1)^n G(n, \tau)\ ,$$

where ν is the number of nearest filaments, and $G(n, \tau)$ is the one-dimensional pair correlation function for imaginary time. As in the previous example we must know the purely one-dimensional correlation function in order to determine T_{cr}. The equation for T_{cr} is more complex than that given by the Eising model because H_0 and H_1 are not commutable in this model (in contrast to the Eising model). The parameter T_{cr} is given by the above equation as

$$k_B T_{cr} = C g_{\perp};\ C \sim 1\ .$$

It is interesting to compare the two models in the light of the fact that the Eising model is the limiting case of the lattice model for $g \gg \beta$, i.e. it aims to model the lattice Fermi gas in the dielectric phase (at $T = 0$) which was discussed above. Thus the two examples considered here describe the three-dimensional ordering of filaments in dielectric or in metallic phases (at $T = 0$). From the corresponding expressions for T_{cr} we note that the transition temperature is substantially higher for filaments in the dielectric phase.

We should stress that the self-consistent method described above can also be used to find approximate expressions for the quasi-one-dimensional correlation functions in an ordered (three-dimensional) phase.

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Physical Properties and Applications of Langmuir Monomolecular and Multimolecular Structures

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The physicochemical and physical properties of monomolecular and multimolecular structures obtained by the Langmuir-Blodgett method are surveyed. Attention is concentrated on the examination of the microscopic picture of the phenomena underlying the applications of these structures in optoelectronics and micro-electronics.
The bibliography includes 122 references.

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I. INTRODUCTION

This review deals with the problem of the creation of complex molecular assemblies by the consecutive transfer of one monomolecular layer of organic molecules after another from the surface of water onto solid supports. A three-dimensional multimolecular structure is thus obtained, whose properties can be specified by the experimenter at will at least along one direction (perpendicular to the plane of the layers). It is striking that with the exception of one translated article[1] which has also become appreciably obsolete, there are apparently no reviews on this subject in the Russian language. Nevertheless, during the last two decades approximately 1000 communications, including several tens of reviews (see, for example, Refs.2–12), a special issue of the journal Thin Solid Films (1980, **68**, No.1) and a monograph[13]† have been published on this question. Molecular or supermolecular construction[9], molecular engineering[11], molecular and biomimetric electronics[8], and the creation of synthetic "organisates"[6]—these apparently constitute what is still an incomplete list of names given to this new branch of research in the field of the physics and chemistry of organic matter. We shall call this branch of science "molecular architectural design" which we believe fully reflects its essential features.

The history of such investigations began with an early study by Franklin[4,14], who carried out numerical estimates of the area of an oil film spreading on the surface of water and observed the suppression of waves in a small lake induced by the film. The results of first systematic studies on the surface tension of water contaminated by organic substances were obtained by Pockels[15]. Subsequently Rayleigh himself carried out a series of studies on the contaminated surface of water and arrived at the following fundamental conclusion[16]: "evidently the observed phenomena are outside the framework of the Laplace theory in which the medium is assumed to be continuous and their explanation requires a molecular approach".

Credit for the determination of the monomolecular nature of the layers at the liquid–gas interface is due to Langmuir. He was the first to establish the possibility of the transfer of monolayers from the surface of water onto solid supports[17]. Subsequently Blodgett perfected this technique and developed a method for the preparation of multilayer structures[18,19]. At the present time the term "Langmuir films" or "Langmuir–Blodgett films" is generally accepted and refers to monomolecular and multimolecular layers transferred from the surface of water onto a solid support.

The idea of molecular architecture, i.e. the creation of complex molecular assemblies with a predetermined architecture in order to obtain specific electrical and optical characteristics, is apparently due to Kuhn. Extensive studies on the optical[2,3] and photoelectric[5–7] properties of the Langmuir multistructures incorporating dye and phosphor molecules were carried out under his supervision in Göttingen in the 1960's–1970's. During very recent years, active studies designed to create molecular assemblies have been prosecuted by the Xerox Company (Canada)[9,12], at a number of English universities[10,11], and also in Japan[8]. There exist also Soviet publications on this topic (see, for example, Refs.20–23).

Nowadays molecular architectural design has aroused the interest of investigators in most varied branches of science. From the standpoint of physics, it gives rise to the possibility of investigating the properties of two-dimensional solid and liquid-crystal structures and microscopic interactions of molecules at rigorously controlled distances from one another and with a rigorously controlled mutual orientation. From the standpoint of chemistry, the possibility of studying the anisotropy of the reactivity of molecules and also of carrying out chemical reactions with molecules fixed in a specially selected matrix are of interest.

For biology, monomolecular and multimolecular structures are primarily systems which model cell membranes. For engineers working in the field of electronics, molecular architecture opens the way to the creation of fundamentally new instruments with spatial resolution at the molecular level by analogy with biological structures[7,8]. The Langmuir method (and also its variant using the adsorption of molecules from solution) is at present one of the most promising ways of creating molecular assemblies and it undoubtedly has a great future.

In the present review, attention is concentrated on the properties of monomolecular and multimolecular layers deposited on solid supports. We shall therefore scarcely discuss the behaviour of monolayers on the surface of water and the general problems of the application of surfactants.

† See also Thin Solid Films, 1983, **99**, Nos.1–3, 1.

These problems have been examined in detail in a monograph[24]. Nor shall we be concerned with the properties of artificial lipid double layers to which an extensive literature has been devoted[25,26]. We have endeavoured to devote much space to the discussion of new ideas having a direct bearing on molecular architectural design avoiding the quotation of numerous specialist investigations. Instead the reviews already mentioned will be widely used[2-12].

Certain compounds used in molecular architectural design.

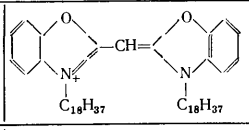
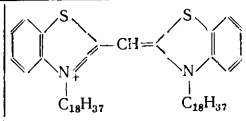
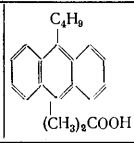
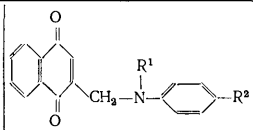
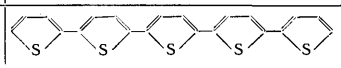
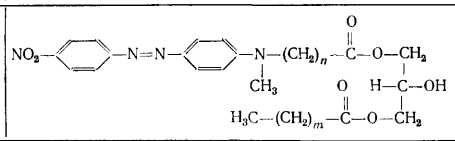
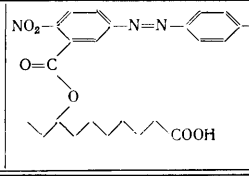
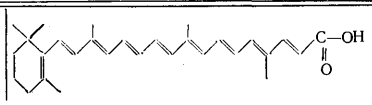
No.	Chemical formula	Name	Refs.	Remarks
(I)	$CH_3(CH_2)_nCOOH$	aliphatic acid	[1]	classical objects for the preparation of Langmuir films
(II)	$CH_3(CH_2)_{16}COO\diagdown\ \diagup Ba^{2+}$ $CH_3(CH_2)_{16}COO\diagup$	barium stearate	[1]	ditto
(III)	$C_{17}H_{35}COOCH_3$	methyl stearate	[28]	stable Langmuir films
(IV)	$CH_3(CH_2)_{14}COO-CH_2$ $CH_3(CH_2)_{14}COO-CH_2$ $(CH_3)_2N-(CH_2)_2(PO_3)-O$	dipalmitoylphosphatidylcholine (artificial lecithin)	[29, 30]	model compound for artificial two-layer membranes
(V)	$(CH_3)(CH_2)_n-C\equiv C-C\equiv C-(CH_2)_nCOOH$	diacetylene derivatives	[10, 11]	compounds polymerising on irradiation with ultraviolet light
(VI)		3,3'-dioctadecyloxacyanine	[2, 6, 33]	(1) energy donor; (2) dichroism on the cleavage plane of crystalline gypsum
(VII)		3,3'-dioctadecylthiacyanine	[6]	energy acceptor, electron donor
(VIII)		10-anthryl-9-butylpropionic acid	[34]	electrophosphor
(IX)	 $R^1 = H,\ R^2 = OC_{18}H_{37};\ R^1 = C_{14}H_{29},\ R^2 = H$	autocomplexes based on 1,4-naphthoquinone	[35]	donor-acceptor properties, intramolecular charge transfer
(X)		quinquethienyl	[85]	dichroism
(XI)		3-*o*-acyl-1-*o*-ω-(*N*-methyl-4'-nitrophenylazophenylamino)acylglycerol	[5, 32]	conformational transitions
(XII)		12-(4'-dimethylamino-4-nitroazo-3-benzoyl)stearic acid	[31, 32]	"molecular conductor"
(XIII)		trans-β-apo-8'-carotenoic acid	[56]	ditto

Table Cont'd...

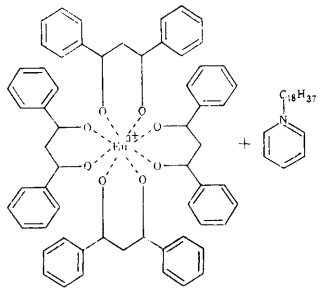
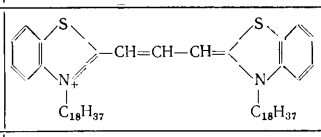
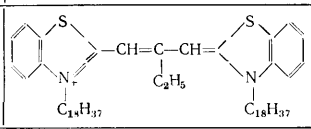
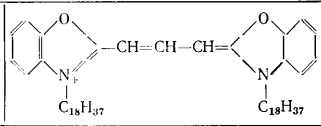
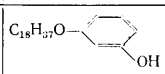
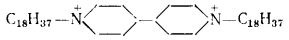
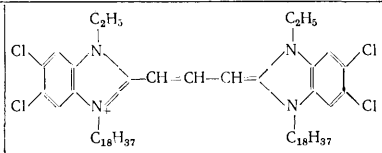
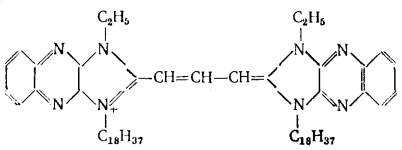
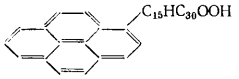
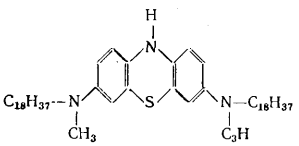
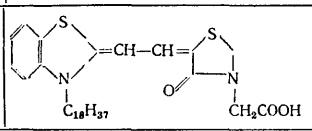
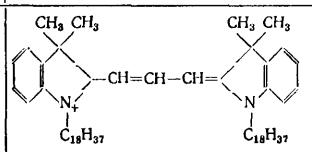
No.	Chemical formula	Name	Refs.	Remarks
(XIV)		mixture of *N*-octadecylpyridine with the dibenzoyloctane complex of europium	[3]	luminescence
(XV)	$C_{18}H_{37}O-C_6H_4-N=N-C_6H_4-R$ $R=SO_2NH_2$, COOH, CN и др.	*p*-substituted derivatives of octadecyloxyazobenzene	[23]	"spontaneous" polarisation
(XVI)		[bis(3-stearylbenzoxazole(2)] trimethinecyanine	[6, 31]	energy acceptor
(XVII)		9-ethyl-3,3'-dioctadecylthiacarbocyanine	[33]	dichroism on the cleavage plane of a crystal
(XVIII)		[bis(3-stearylbenzoxazole(2)] trimethinecyanine	[1]	energy acceptor
(XIX)		*m*-octadecyloxyphenol	[80]	pyroeffect
(XX)		distearylbipyridylium salt (viologen)	[6]	electron acceptor
(XXI)		5,5',6,6'-tetrachloro-3,3'diethyl-*N,N'*-dioctadecylbenzimidocarbocyanine	[2]	electron donor
(XXII)		3,3'-diethyl-*N,N'*-dioctadecylbenzopyrazinoimidocarbocyanine	[6]	electron acceptor
(XXIII)		ω-1-pyrenylpalmitic acid	[5]	electron acceptor
(XXIV)		leuco-form of Stearylene Blue	[5]	electron donor

Table Cont'd...

No.	Chemical formula	Name	Refs.	Remarks
(XXV)		5-[1'-(3''-octadecyl-2''-benzothiazolinylidene)ethylidene-2'-rhodanine] 3-acetic acid	[87]	photoconduction sensitiser
(XXVI)		*N,N'*-dioctadecylindocarbocyanine	[54]	electron donor

II. PHYSICOCHEMICAL ASPECTS AND TECHNIQUE OF THE PREPARATION OF MONOLAYERS AND MULTILAYERS

1. Amphiphilic Compounds

In order to obtain Langmuir films from any one substance, it is in the first place necessary that it should form stable monomolecular layers on the surface of water. This condition is as a rule satisfied by molecules with a polar hydrophilic "head" and a long lipophilic (i.e. soluble in fats or hydrophobic) hydrocarbon "tail". Such molecules are called biphilic or amphiphilic.

Classical examples of amphiphilic compounds are aliphatic acids [see, for example, compound (I) in the Table] or their salts (soaps) [compound (II)]. The polar heads of these molecules are smoothly incorporated in the local water structure (we have in mind the short-range structural order). On the other hand, the hydrophobic hydrocarbon tails are not incorporated in the water structure, since the hydrogen bonds in liquid water would have to undergo a rearrangement to avoid falling within the region occupied by the hydrocarbon tail; such a structural rearrangement decreases the entropy of the system and is therefore unfavourable. Thus the hydrophobic effect does not presuppose the presence of any special repulsion forces between water and hydrocarbon molecules and appears solely due to the mutual attraction of the water molecules leading to the "expulsion" of the hydrocarbon to the outside[27]. As a result, a monolayer of molecules of the amphiphilic substance, whose hydrocarbon tails are "forced out" into the gas phase while the polar heads are in the liquid phase, arises on the surface of water. A small proportion of the molecules are then in the bulk of the liquid, since the solubility of amphiphilic compounds in water is usually 10^{-6}–10^{-10} M depending on the length of the hydrocarbon tail: an increase in the length of the tail by two carbon atoms reduces the solubility approximately by an order of magnitude.

Apart from aliphatic acids and their salts, stable monolayers on the surface of water are formed by ethers[28], the phospholipids used to obtain artificial two-layer membranes[29,30], certain diacetylenes capable of polymerisation[10,11], and also a number of dyes[31–33], aromatic compounds[34], and autocomplexes[35] with a wide variety of structures but virtually always possessing a long hydrocarbon chain (quinquethienyl is an exception[85]). Examples of the corresponding compounds are presented in the Table [see compounds (III)–(XII)].

There exist also a series of biologically active compounds such as cholesterol, chlorophyll, various proteins, etc., which form monomolecular layers capable of being transferred from the surface of water on to solid supports[1]. Many compounds which do not form monolayers themselves are readily incorporated in the structure of Langmuir monolayers of other compounds, in particular aliphatic acids. Examples of dyes of this kind are quoted in a review[2].

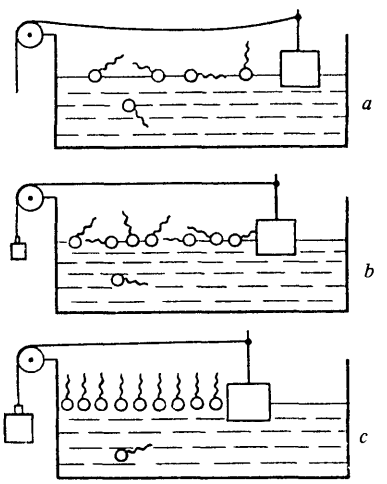


Figure 1. The molecules of an amphiphilic compound on the surface of water: *a*) in the two-dimensional "gaseous" phase; *b*) in the two-dimensional "liquid" phase; *c*) in the two-dimensional "liquid crystal" phase.

2. The Polymorphism of Monolayers

At a low concentration of the amphiphilic compounds on the surface of water the monomolecular layer is not continuous (Fig. 1*a*). Their molecules hardly interact, their tails above the surface of water are oriented at random, and such a phase may be regarded as a two-dimensional gas by analogy with the usual gas phase. If the surface area occupied by the amphiphilic molecules is reduced by means of a floating barrier, they initially approach one another but remain oriented at random (Fig. 1*b*). Such a phase may be called a two-dimensional liquid. With increase of pressure from the

side of the floating barrier, the amphiphilic molecules acquire orientation order but retain the ability to migrate within the plane of the layer. There is then no long-range positional order and the new phase is a two-dimensional liquid crystal (Fig. 1c) equivalent to one (polar) layer of a smectic liquid crystal[36,37]. Further increase of the surface pressure leads to the "puckering" of the monolayer or its collapse. In certain cases after the collapse there is a possibility of two-, three-, or four-layer structures[38].

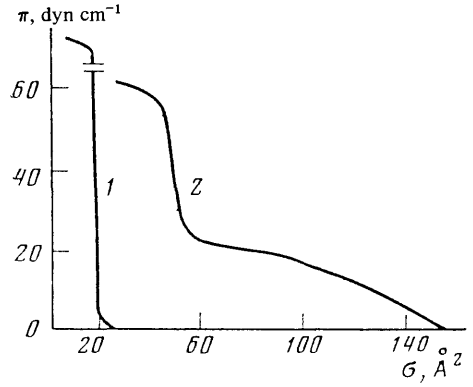


Figure 2. The π–σ isotherms for arachidic acid (curve *1*) and the dye (VII) (curve *2*).[2]

The sequence of phase transitions or the polymorphism of the monolayer can be investigated by following the relation between the surface pressure and the area occupied by the monolayer. Here there is an analogy with the equation of state for a normal three-dimensional substance and one usually measures π–σ isotherms, where π is the surface pressure in dynes per unit length of the floating barrier and σ is the area per molecule. Examples of such isotherms are presented in Fig. 2 for arachidic acid [compound (I) in Table, $n = 18$] and a dye (VII) which has two hydrocarbon chains attached to the side of the chromophore. It is clearly seen from Fig. 2 that from the very beginning the arachidic acid molecules occupy an area approximately equal to the cross-sectional area of the hydrocarbon chain (approximately 20 Å²), i.e. they virtually "stand" vertically on the surface of water. The transition from the "gas" phase to the "liquid crystal" phase takes place almost instantaneously, by-passing the "liquid" phase. For the dye (VII), the situation is different: before the hydrocarbon tails stand at right angles to the surface (to which $\sigma = 50$ Å² corresponds), there is a gradual growth of the surface pressure reflecting the interaction of the molecules which have not yet been oriented ("liquid" phase). In fact the isotherm for the dye (VII) shows two phase transitions, one at $\sigma = 150$ Å², which is approximately equal to the area of the molecule with the hydrocarbon chains lying on the surface of water, and the other at $\sigma = 50$ Å², which corresponds to the cross-sectional area of two vertically oriented chains. Furthermore, curve *2* (Fig. 2) reveals the collapse of the monolayer at $\sigma = 30$ Å².

A more complex example of polymorphism is presented in Fig. 3. According to Heeseman[32], a rearrangement of the conformation of the molecule of the azo-dye (XI) with increase of surface pressure may be observed. The molecular geometries are illustrated schematically in Fig. 3 in the corresponding part of the isotherm.

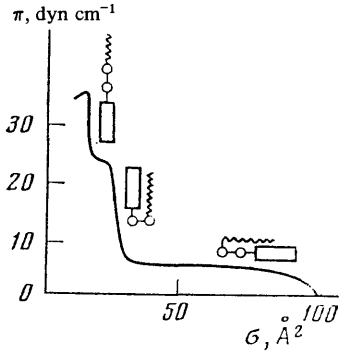


Figure 3. The polymorphism of a surface-active azo-dye (XIII) monolayer. Rectangle—azo-fragment; circles—ester groups; wavy lines—hydrocarbon chains[32].

At a specified temperature it is possible to achieve the required phase state of the monolayer by specifying a particular surface pressure. This can be done automatically by establishing an electrical connection between the motor moving the barrier and the surface pressure measuring device. The latter usually consists of a Wilhelmy balance, which measures the surface tension (the surface pressure is the difference between the surface pressures of the clean water surface and the surface covered by a monolayer of the surfactant).

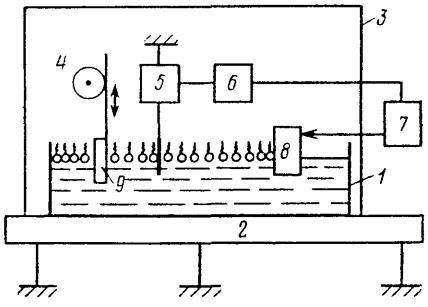


Figure 4. Device for the deposition of Langmuir–Blodgett films: 1) bath; 2) stand on shock absorbers; 3) protecting jacket (transparent); 4) mechanism for the raising and lowering of supports *9*; 5) Wilhelmy electric balance; 6) motor control circuit; 7) motor controlling the mobile barrier *8*.

3. The Langmuir–Blodgett Method

In order to obtain a monolayer, the surfactant is dissolved in a volatile solvent (for example, in chloroform) and is deposited dropwise on the surface of specially purified doubly

distilled water. The solution spreads on the surface and the solvent volatilises. The residual surfactant is compressed by the floating barrier until a continuous film is obtained. The instant of the attainment of the liquid crystal phase state of the monolayer can be detected by means of the Wilhelmy balance; after that one monolayer after another is transferred in succession onto the solid support. This requires the application of a mechanical device, which slowly (at a rate of several mm per minute) lowers or raises the solid support through the surface of the monolayer[17,18]. As the monolayers are deposited consecutively onto the support, the amount of substance on the surface of water naturally diminishes and the floating barrier must be moved automatically to keep the surface pressure constant. The general schematic illustration of the corresponding apparatus is shown in Fig. 4.

Depending on the direction of motion of the support through the monolayer, it is possible to obtain Langmuir films with different orientations. Usually three types of layers are distinguished: two polar layers of types *X* and *Z* and one symmetrical non-polar layer of type *Y* (Fig. 5). In order to deposit the first monolayer of type *X* or *Z*, the support must be hydrophobic or hydrophilic respectively. It is noteworthy that multilayers of type *X* or *Z* cannot always be obtained by the experimenter at will. In many instances, for example, when attempts are made to obtain layers of the *X* type with aliphatic acids, *Y* layers are obtained. This means that the molecules can "capsize" during the deposition of the monolayer. The mechanism of the capsizing process is at present unknown although numerous studies are being devoted to it[1,39]. In general the technique of preparation of Langmuir films still requires much skill from the experimenter, because the quality of the films is influenced by an unduly large number of factors, among which the most important are (a) the purity of water and general cleanliness of the apparatus, (b) the pH of the buffer (i.e. aqueous) solution, (c) the temperature, (d) the preparation of the support, (e) the rate of deposition and variation of the surface pressure, and (f) the absence of mechanical vibrations in the system.

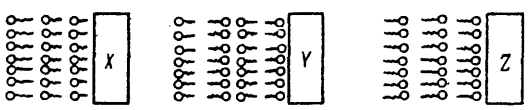


Figure 5. Types of multilayers obtained in accordance with the direction of motion of the plate through the surface of water.

X-Ray diffraction and electron diffraction studies have shown that the Langmuir films frequently have a solid crystal structure[1,40]. This means that, in the course of the deposition of the film, the substance as a rule crystallises although it may be in a vitreous state. However, the orientational order in a liquid crystal phase, including the polar order, persists in the solid crystal phase (with the exception of the case of the capsizing of molecules already mentioned). Thus one obtains ultimately solid multilayer layers with a predetermined composition, thickness, and orientation. This constitutes the uniqueness and value of the Langmuir–Blodgett technique.

In recent years the Langmuir method has been appreciably improved. For example, successful attempts have been made to obtain multilayers of different molecules. Double[41] and also multisector[42] baths, permitting the automatic transfer of supports from one solution to another and conversely, have been developed for this purpose. This increases sharply the productivity of the apparatus and in addition permits the avoidance of the contamination of the specimens.

4. Other Methods of Preparation of Multilayer Structures

Stable monomolecular layers on solid supports can also be obtained by the adsorption of surface-active molecules from the liquid phase[43]. For example, solid films of aliphatic acids or their perfluoro-derivatives are easily adsorbed on glass covered with aluminium or nickel and immersed in a solution of these acids in hexadecane[5]. Monolayers of trichloro-n-octadecylsilane can also be obtained by adsorption. Successive repetition of this procedure can give rise to a multimolecular layer. This method is technically simpler than the Langmuir method but it imposes more stringent requirements on the structure of the corresponding molecules. Monomolecular layers of aliphatic acids on solid supports can be obtained in principle also by the thermal sputtering method[4].

The introduction of surface-active dyes into the solution already containing aliphatic acid molecules can yield mixed monolayers in which the dye molecules are incorporated in the matrix of aliphatic acids. With the aid of another solvent, it is possible "to wash out" the dye molecules selectively from the monolayer leaving behind the so-called skeletised monolayer. Skeletised monolayers possess a "memory" of their initial structure, which can be restored by the readsorption of the same dye or another one with a suitable molecular geometry.

Monolayers and multilayers prepared by the Langmuir technique can be transferred from one solid support to another by the contact method illustrated schematically in Fig. 6[6,7]. For example, a flexible poly(vinyl alcohol) film can be conveniently used as the second support[2]. It is of interest that the information recorded on one support (in the form of, for example, a certain distribution of dimers and monomers) can be "copied" onto another plate[7].

III. ELECTRICAL PROPERTIES OF LANGMUIR FILMS

1. Dielectric Characteristics

Fairly numerous studies have been made for the dielectric properties of multimolecular layers in view of their wide scale employment as calibrated dielectric plates in transistors based on metal–dielectric semiconductor structures[11]. Stringent requirements must be met by the dielectric plates as regards the reproducibility of their capacitance, stability, and resistance to electrical breakdown.

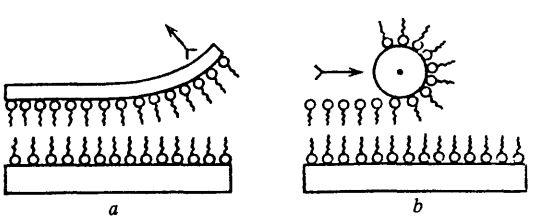


Figure 6. Illustration of the principle of the separation (*a*) and contact deposition (*b*) of a monolayer[7].

The dielectric properties of Langmuir films are usually investigated in sandwich structures with a lower aluminium electrode. The aluminium is deposited by vacuum sputtering onto a glass support, the multimolecular layers are introduced in succession, and then the upper metallic electrode is deposited by vacuum sputtering. The lower electrode can also consist of a sputtered tin film[44] or transparent semiconducting layers of tin dioxide[23], as well as other semiconducting materials[11]. The application of other metals (other than tin and aluminium) frequently leads to non-reproducible results. The Langmuir films exhibit poor adhesion to noble metals.

Carefully prepared (defect-free) sandwich structures usually withstand the application of electric fields up to 5×10^6 V cm^{-1}, which is characteristic of the best of the known dielectrics[45,46]. The reciprocal of the capacitance C^{-1} of the sandwich structures varies linearly with the overall thickness of the multilayer regardless of whether the number of monolayers (Fig.7*a*) or the thickness of each monolayer (Fig.7*b*) are varied.

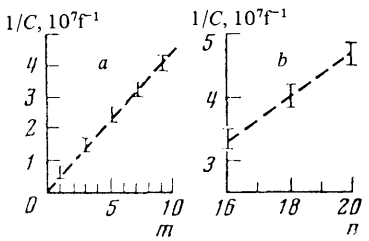


Figure 7. *a*) Dependence of the capacitance of a multilayer palmitic acid structure (number of carbon atoms $n = 16$) on the number of monolayers[8]; *b*) dependence of the capacitance of a seven-layer structure on the length of the aliphatic acid molecule with $n = 16-20$ (frequency 10^{-2} Hz; 300 K)[8].

The absolute dielectric constants of aliphatic acids at low frequencies are $\varepsilon = 2.5-2.9$ at 77–295 K.[43] Dielectric constants close to the above values of ε are expected also for dyes with hydrocarbon tails. For perfluoro-derivatives of aliphatic acids, the dielectric constants are appreciably higher ($\varepsilon = 2.9-3.5$ at $T = 77-295$ K)[43].

As frequency is varied, dispersion of ε is observed, which can be attributed to relaxation processes of different types. At frequencies below 1 Hz the slow movements of the polar COOH groups are apparently responsible for the mechanism of the relaxation of ε for aliphatic acids, while at frequencies in excess of 1 Hz the processes associated with jump movements of electrons from one monolayer to another are responsible for the relaxation[47,48]. The presence of residual water in the multilayer leads to an additional mechanism of dielectric losses[49].

2. Electrical Conductivity

At the present time there are no firmly established ideas about the mechanisms of the flow of electric current through metal–dielectric–metal structures, where the Langmuir film plays the role of the dielectric. At a specified potential at the electrodes, the current depends markedly on the thickness of the multilayer, the material of the electrodes, the temperature, the surrounding atmosphere, and naturally the material of the multilayer itself. In the latter case the presence or absence in the multilayer of molecules with a long chain of conjugated bonds plays a significant role.

The case of extremely thin films, with a thickness equivalent to one or two monolayers (which corresponds to 25–50 Å for aliphatic acids), is apparently simpler. The majority of investigators believe that the dominant mechanism of the conduction of current at temperatures in the range from room temperature downwards is tunnelling of electrons through the monolayer[45,46,50–52]. Fig.8 illustrates instances of the tunnel electron transition from one electrode to another through a potential barrier at a potential applied to the electrodes smaller and greater than the height of the barrier[52]. A characteristic feature of the tunnel mechanism is the absence of a dependence of the current on temperature and the exponential decrease of the current with increase of the thickness of the monolayer; the latter can be varied by passing from the lower homologues of aliphatic acids ($n = 14$) to higher homologues ($n = 20$). The thickness of the monolayer then changes from 21 to 28 Å and the effective conductivity diminishes approximately by 5 orders of magnitude[50]. The tunnel current is influenced significantly also by the presence of an oxide film on the metal surface; allowance for this influence is essential in the calculation of the characteristics of the energy barrier for the tunnelling electrons[46].

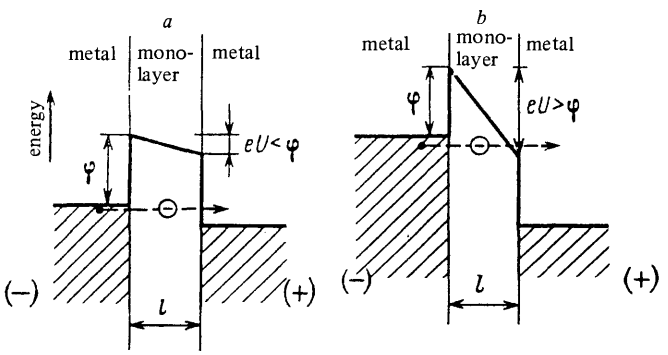


Figure 8. The tunnelling of an electron through a potential barrier at electrode potentials $U < \phi/e$ (*a*) and $U > \phi/e$ (*b*); ϕ = height of barrier; l = thickness of monolayer.

The flow of current through two monolayers in succession is apparently determined also by the tunnel mechanism at least at low temperatures[29]. In the presence of a larger number of monolayers, other processes begin to play an appreciable role. The most probable of these is the jump electron transfer mechanism. Its essential feature is as follows. It is believed that at the boundaries of the monolayers there are large numbers of surface energy states. The electron apparently moves across the multilayer from the negative electrode to the positive electrode not via a single tunnel transition (which would be already extremely unlikely when the number of monolayers exceeds three) but in separate small jumps (a jump constitutes tunnelling accompanied by thermal excitation) through each monolayer in succession (Fig.9). In this model the current decreases exponentially with increase of the thickness of each monolayer separately but with increase in the number of identical monolayers it diminishes merely in accordance with a linear law. This conclusion is in full agreement with experiment[8,53]. The picture illustrated in Fig.9 becomes appreciably more complex when

account is taken of the curvature of the barrier due to the charges bound at the boundaries between the monolayers; this effect has been taken into account[54].

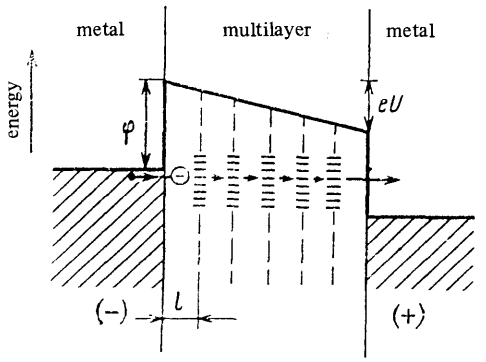


Figure 9. The jump mechanism of the electrical conduction in multilayers (l = thickness of monolayer).

Together with the jump conductivity, injected carriers associated with the emission of electrons from the electrode into the bulk of the multilayer via a contact potential barrier may make an appreciable contribution to the current[52]. This mechanism (the Schottky emission) can apparently explain the marked influence of the material of the terminals on the conductivity of the metal–Langmuir film–metal system. Nor can one rule out the possibility of the ionisation of the impurity molecules in the bulk of the multilayer by the electric field (the Poole–Frenkel mechanism)[52]. The latter effect may play a dominant role in relatively thick multilayers (tens of monolayers).

In the multilayers formed by molecules of substituted anthracene [see, for example, compound (VIII)], a sharp anisotropy of the electrical conductivity is observed. For the same electric field strength, the conductivity in the plane of the multilayer can exceed by 8 orders of magnitude the conductivity measured at right angles. The anisotropy has been explained[55] by a special type of packing of the molecules of compound (VIII) in the monolayer (like a deck of cards), which facilitates the transfer of electrons from molecule to molecule in the plane of the monolayer. However, one should also take into account the possibility of conduction via interlayer surface states, which has also been noted[8]. The passage of the current along the monolayer in the latter case does not require an activated electron jump through relatively wide barriers and the current should be significantly greater for the field directed along the plane of the monolayers.

The introduction of molecules with an extensive chain of conjugated bonds as impurities into the aliphatic acid monolayer increases the tunnel current for the monolayer. Such an experiment has been carried out[56] using carotenoic acid (XIII). Figuratively speaking, the molecules of this acid play the role of thin "conductors" which partially "short circuit" the aliphatic acid monolayer, because they have a free electronic level located below the energy level of an electron *in vacuo*, which facilitates electron tunnelling. In fact the molecules with conjugated bonds lower the height of the potential barrier for the tunnel transition. The molecules of azo-dyes (XII), whose conjugated chain is oriented at right angles to the plane of the monolayer, also influence the conductivity in a similar manner[31]. As stated above, adsorbed monolayers[43,57] can be "skeletised" by desorbing the dye molecules introduced into the monolayer beforehand. The resulting holes are responsible for the marked (approximately by an order of magnitude) increase of the tunnel current through the monolayer[51], although there is no short circuiting as a consequence of the holes being "overgrown" by a layer of the oxidised material of the electrode.

3. Inelastic Tunnelling and Tunnel Spectra

Direct proof of the tunnel mechanism for the flow of current through individual Langmuir layers is provided by the observation of the tunnel spectra of impurity states. Fig.10 illustrates elastic (1) and inelastic (2) electron tunnelling through a dielectric layer. In the latter case the tunnelling electron loses its energy on passing through the film, liberating a molecule of the main substance of the dielectric or impurity. Usually one is dealing with vibrational molecular excitations[58] and $W \cong 0.1$ eV, since the energies of the tunnelling electrons (in eV) do not exceed numerically the potentials (in volts) applied to the electrodes. However, electronic transitions with energies $W \cong 1-2$ eV can also be excited[59]; the loss of energy by the electron under these conditions gives rise to a small (~1%) anomaly on the voltage–current characteristic at an electrode potential $U = W/e$ (Fig.11*a*). If the $I-U$ curve is differentiated twice with the aid of an electronic circuit, the anomaly is revealed extremely clearly (Fig.11*b*). In the presence of a large number of varied energy states within the monolayer, the d^2I/dU^2 curve represents an elaborate spectrum of bands.

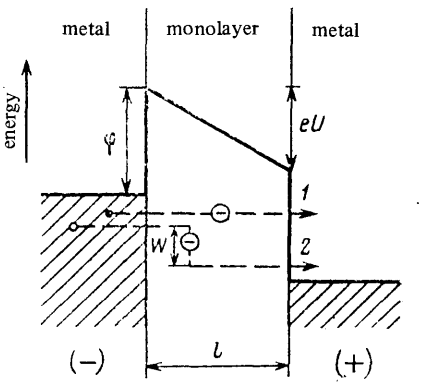


Figure 10. The elastic (curve *1*) and non-elastic (curve *2*) tunnelling of an electron through a monolayer.

The tunnel spectra can reflect the electronic structure not only of the dielectric but also the metal. In particular, the spectra reveal the energy gap characteristic of a superconductor, provided that even only one of the electrodes is a superconductor (the experiment was carried out below the critical temperature). Such observations have been made using the barium stearate monolayer as the dielectric layer[60]. The vibrational spectra of the stearic acid monolayer, obtained recently by tunnel spectroscopy, agree well with infrared and Raman spectra[61]. One cannot rule out the possibility that the method of tunnel spectroscopy will prove

suitable also for the investigation of the electronic spectra of molecules with conjugated bonds forming Langmuir or adsorption monolayers or behaving as impurities in the latter, since at low temperatures such monolayers do not undergo electrical breakdown at potentials up to 4 V,[51,60] while electronic spectra correspond to energies ≥ 1 eV.

A fairly detailed review of the electrical properties of Langmuir layers, including a discussion of the mechanisms of their electrical conduction and breakdown, has been published[62].

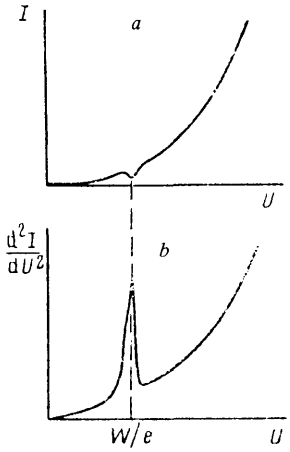


Figure 11. The determination of the characteristics of the tunnel "spectrum" with the aid of the differentiation of the voltage–current characteristic.

4. Asymmetric Structures and a Molecular Rectifier

If the electrodes with a multilayer structure are made from different metals, then in the case of symmetrical multilayers of the *Y* type (see Fig.5), a potential difference appears in the specimen as a consequence of different electronic work functions of the metals. Such a potential difference can arise even in the presence of identical (for example, aluminium) electrodes due to the different properties of the outside film on the lower and upper electrodes[63]. The potential difference due to the difference between the electronic work functions usually amounts to tenths of a volt. If approximately 200 such specimens are connected in series, then a potential of 50 V can be drawn from a battery obtained in this way[60].

It has been claimed[54] that the difference between the electron work functions leads to the electrical breakdown of sandwich structures even in the absence of an external field, provided that they consist of a single aliphatic monolayer between aluminium and barium electrodes.

Another type of asymmetry can be created by the successive deposition of monolayers of different compositions; the material of the electrodes can then be identical. For example, an unusual form of the tunnel voltage–current characteristic, corresponding to the passage of current through a three-layer structure in only one direction, has been predicted theoretically[64]. It is significant that in this case one of the monolayers must be formed by surface-active donor molecules and the other by acceptor molecules, so that the multilayer is in fact an analogue of a charge-transfer complex in which the donor and acceptor are separated by a narrow neutral bridge [the molecules of the autocomplexes (IX) are good models]. The electron current flows along the acceptor–neutral bridge–donor chain from one electrode to the other with non-elastic tunnelling in the neutral bridge. The reverse current is much smaller and the authors[64] thus predict a current rectifying effect.

So far as we are aware, there are no published experimental data concerning the observations of the predicted effect apparently owing to the difficulty of observing the tunnel current in a three-layer, i.e. relatively thick, structure. However, the rectifying effect has been noted for a photocurrent in asymmetric donor-acceptor multilayers[54]. The attempts to create specifically rectifying and subsequently also transistor multistructures may serve as classical examples of molecular architecture.

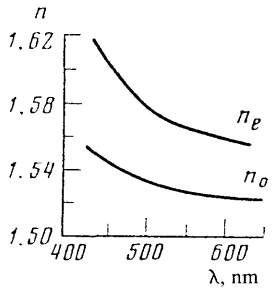


Figure 12. The dispersion curves for the refractive indices of cadmium arachidate[65].

IV. THE OPTICAL PROPERTIES OF MONOLAYERS AND MULTILAYERS

1. Reflective Indices

Langmuir films are specially interesting from the standpoint of the creation of multilayer structures for the investigation of various interference phenomena, because the thickness of a single monolayer is rigorously fixed (it amounts to 24.5 Å for barium stearate, for example[1]). Numerous studies have been made on the optical properties of multimolecular layers formed by aliphatic acid salts[1,3]. The ellipsometric method, measurements of optical transmission and reflection, interferometry and, recently, the integral-optical technique have been widely used for this purpose[10]. The optical anisotropy of multilayers has been reliably established: the refractive index for light with its polarisation vector in the plane of the multilayer (n_o) is always less than the refractive index for polarisation whose direction coincides with the normal to the film (n_e). The optical anisotropy for cadmium arachidate for example, is fairly considerable ($\Delta n = n_e - n_o \cong 0.04$). Virtually no systematic studies of the frequency dispersion of n_e and n_o have been made and reliable data are available only for cadmium arachidate multilayers (Fig.12)[65].

There exist two possibilities of adjusting n_e and n_o to prespecified values at a particular wavelength. Firstly, by varying the composition of the buffer solution, it is possible

to obtain films of salts of different metals (Cd, Ba, Mn) alternatively films made up of aliphatic acid molecules with different lengths of the hydrocarbon chain can be used. The presence of atoms of heavier metals then increases both refractive indices n_o and n_e, while an increased hydrocarbon chain length entails mainly an increase of n_e. The pH of the buffer solution also plays a significant role, determining the concentration of the metal ions in the Langmuir film[10]. It is possible to introduce various dyes into multilayers of aliphatic acids and their salts, which also alters the refractive indices. The second method consists in the skeletisation of Langmuir films. The formation of "holes" on a molecular scale lowers the values of n_e and n_o in proportion to the area occupied by these "holes". Both methods are promising for the specific construction of interference coatings, integrated optical elements, etc.

2. The Waveguide Properties of the Films

It is known that the light beam propagated in any medium with a refractive index n_1 undergoes total internal reflection at the boundary with another optically less dense medium ($n_2 < n_1$) if the angle of incidence exceeds a critical value. A light beam introduced into a thin film at a certain angle is therefore propagated along the film as in a waveguide, undergoing repeated internal reflections at the boundaries of the film with air or another medium satisfying the condition $n_2 < n_1$. This phenomenon makes it possible to achieve extremely compact (film) optical elements used in modern integrated optics[66].

The possibility of the specific variation of the refractive indices and the clear-cut determination of their thickness make Langmuir films extremely convenient materials for such purposes. The main difficulty consists in obtaining defect-free films of high optical quality, since otherwise the light beam propagated along the film is to a large extent scattered by defects, losing its intensity. The best results have been obtained currently on cadmium stearate films[10,21]. Such a film (with the refractive indices $n_o = 1.53$ and $n_e = 1.56$ at a wavelength $\lambda = 633$ nm) is deposited on a quartz support ($n_2 = 1.4571$) and is covered on top by a liquid layer of isostearic acid ($n_3 = 1.4573$). Light is introduced into the film with the aid of a prismatic device and is propagated along it with a decay of 1 dB per cm of the length of the film (i.e. is attenuated by a factor of 10 over a distance of 10 cm).

The introduction of additional monolayers absorbing light in a particular spectral range as a result of the presence of surface-active dyes makes it possible to achieve the isolation of specific spatial[67] or spectroscopic[68] components of the radiation.

Langmuir films are also used as external plates of waveguide films, made, for example of glass or poly(methyl methacrylate)[65]. In this case the geometrical properties of the beam in the waveguide (modal composition) contain information about the refractive indices of Langmuir films consisting of a small number of monolayers. The method based on the measurement of the decay of surface electromagnetic waves propagated along the boundary between dielectric and metal is even more sensitive to the optical characteristic of individual monolayers. Such waves can be excited by visible[68] or infrared[69–71] radiation.

3. Molecules "in front of a Mirror"

Molecular architecture leads to an interesting possibility of investigating a wide variety of optical interference effects. In fact we can achieve the alternation of light emitting, reflecting, and absorbing layers in accordance with a predetermined plan with a rigorous specification of their thickness in each case. If the thicknesses of the corresponding layers are comparable to the wavelength of the light, it is possible to observe a whole range of new phenomena determined by the interference and diffraction of light[3].

Suppose, for example, that a light beam is incident on a metallic mirror surface (Fig.13). The reflected wave interferes with the incident wave, giving rise to a standing wave whose nodes and antinodes are located at fixed points in space. We now imagine that a molecule of a fluorescent dye is placed at different distances from the mirror surface. Then the molecules located at the antinodes of the standing wave will fluoresce strongly, while those which are at the nodes will not fluoresce at all. Such an experiment makes it possible to discover the location of the nodes of the standing wave, which depends on the phase of the beam reflected from the mirror. Classical experiments of this kind were performed as early as the past century by Drude and Nernst using photographic emulsions as indicators of the intensity (i.e. the square of the amplitude) of the standing wave. Using Langmuir films, such experiments can be carried out with a much higher degree of accuracy.

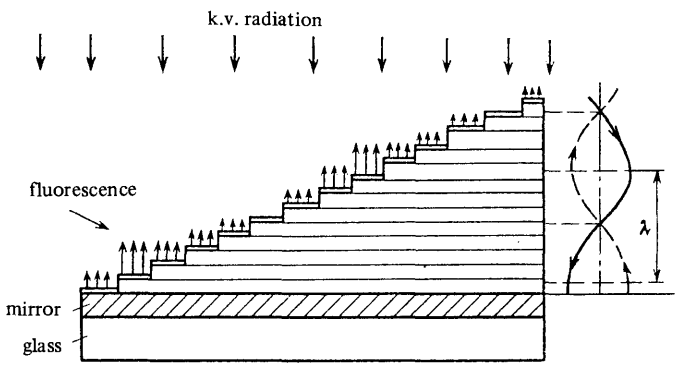


Figure 13. The Kuhn "ladder". Each "step" consists of 20 stearic acid monolayers. One of the monolayers of the fluorescent dye covers all the "steps" at once. The antinodes of the standing light wave (see the scheme on the right) are visualised with the aid of fluorescence; the fluorescence intensity is represented conventionally by the length of the vertical arrows[2].

Fig.13 illustrates the scheme of Kuhn's experiment[2]. Monolayers, for example of cadmium arachidate, were deposited on a silver mirror on a glass support in such a way that each successive monolayer occupied a smaller area than the preceding one; this results in the formation of a "ladder" of monolayers. A single monolayer of a surface-active fluorescent dye [for example, compound (VI)] is then deposited on the entire multistructure. The illumination of the multilayer from above with ultraviolet light at $\lambda = 366$ nm leads to the appearance of a very attractive striped fluorescence pattern of the dye on those sections of the "ladder" which correspond to the antinodes of the standing wave[72].

The light emitted by the fluorescent molecules located at a certain distance from the mirror can also be involved in the interference. The character of the interference then

depends on the nature of the emitter. An electric dipole, a magnetic dipole, an electric quadrupole, etc. are known to be capable of emitting. Each fluorescence band of the dye is associated with its intrinsic emitter so that there is a possibility of the transformation of the complex fluorescence spectrum of the dye as a result of interference effects. An example of such change in the spectrum is illustrated in Fig. 14[3]. The dibenzoyloctane complex of europium (XIV) forms a monolayer separated from a gold mirror by a definite number of cadmium arachidate monolayers. The entire multistructure is immersed in an immersion liquid in order to avoid reflections from its surface. The complex fluoresces on excitation with ultraviolet light. Fig. 14 shows that simple reflection from the mirror alters the form of the spectrum. This implies that the weak fluorescence band with a maximum at 592 nm cannot, in contrast to the band at 615 nm, be attributed to an electric dipole emitter[3]. The proximity of the molecular emitter to the metallic mirror leads to yet another remarkable effect: the fluorescence decay time begins to depend on the distance from the mirror. As a consequence of the interference of the waves, this dependence is oscillatory; when the emitter is in the immediate vicinity of the mirror ($0 < d < 500$ Å), the decay time tends to zero asymptotically.

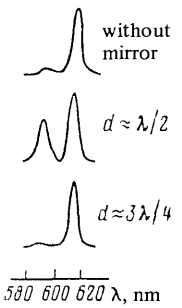


Figure 14. The fluorescence spectrum of a europium complex as a function of the distance d of the molecular emitters from the gold mirror.

By alternating the Langmuir monolayers with metallic mirrors sputtered *in vacuo*, it is possible to create a superlattice having two periods, one of which is equal to the thickness of a single monolayer and the other is equal to an arbitrarily specified distance between the metallic mirrors. The spectroscopic properties of such superlattices agree with theoretical calculations[22].

Numerous other examples of interference effects observed in the optical transmission and interaction of light for different positions of the absorbing or luminescent monolayer in a multimolecular structure have been quoted in reviews[2,3]. The method of specific construction of such multilayers makes it possible to elucidate the nature of the electronic oscillators in molecules.

4. The Dichroism of Dyes

The anisotropy of the refractive indices of Langmuir films was mentioned above. We shall consider the question of the orientation of the chromophoric chains of dye molecules which either form these films or have been introduced into monolayers of aliphatic acids as admixtures. In the usual method of the transfer of monolayers from the surface of water onto a glass or metallised surface, the monolayer or the multistructure on a solid surface is isotropic relative to the rotation of the specimen around the normal z to the layer; the z axis is the only distinct axis. When dyes are introduced into such a multilayer, light is absorbed regardless of the direction of its polarisation if the beam is incident rigorously at right angles to the surface of the multilayer.

On the other hand, chromophoric chains of the dye can be distributed in different ways, being oriented on average either at right angles to the support or in the plane of the support. The situation which is actually realised may be elucidated by studying the anisotropy of the absorption of light for layers placed at a certain angle relative to the incident beam (examples are presented in Fig. 15). In the molecule of the azo-dye (XV) the alkoxy-"tail" is attached to the azo-system in the *para*-position and the entire molecule is oriented at right angles to the plane of the monolayer. Correspondingly light polarised in the plane of incidence (with an electric vector e_1—see the insert Fig. 15) is absorbed more strongly than the light with the vector e_2 in the perpendicular plane, since in the former case there is a component parallel to the conjugation chain of the molecule (Fig. 15*a*). The broad absorption band with $\lambda_{max} \cong 500$ nm in Fig. 15*b* is associated with the polymethine dye (XVI) whose chromophores are located in the plane of the support. In this case the light with the vector e_2, also located in the plane of the support, is absorbed more intensely. The additionally introduced azo-dye (XII), absorbing in the region of $\lambda \cong 415$ nm, has a dichroism with a different sign (the absorption shoulder in the short-wavelength region is weaker), which corresponds to the perpendicular orientation of the chromophore, as in the case illustrated in Fig. 15*a*. The perpendicular orientation of the chromophores has been observed also for other dyes without alkyl tails introduced as admixtures into Langmuir aliphatic acid multilayers[72]. The same orientation of the chromophores of the azo-dyes (XII) in a monomolecular layer on the surface of water (i.e. before its transfer to the support) has also been established[32].

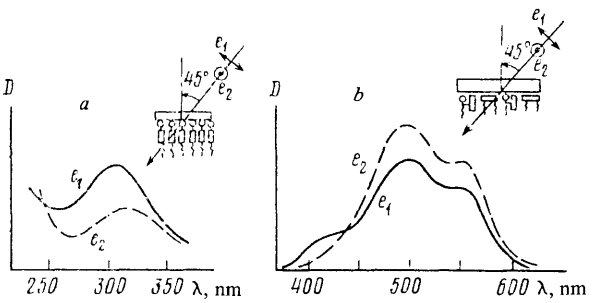


Figure 15. The dichroism of dyes with different orientations of chromophores: a) perpendicular orientation for the azo-dye (XV) with R = SO_2NH_2;[73] *b*) spectra of mixed monolayers of the azo-dyes (XII) and the polymethine dye (XVI) with the chromophore oriented parallel to the support[31]. The inserts illustrate the geometry of the experiment; the rectangles represent molecular chromophores.

A remarkable example of dichroism of another type has been demonstrated in a study[33] where an anisotropic surface (the cleavage plane of crystalline gypsum) was used as the support for the deposition of monolayers. In this case the molecules of the surface-active dyes (VI) and (XVII) are distributed with the chromophores not located simply in the plane of the support but along a specific direction on this plane which coincides with the orientation of one of the crystal axes of gypsum. The dichroism of such monolayers and multilayers can be easily observed also when the beam is incident at right angles to the specimen (Fig.16). The light polarised parallel to the *a* axis of the gypsum crystal is absorbed much more intensely, which indicates the orientation of the chromophore of the dye (XVII) precisely along the *a* axis. The above study[33] thus leads to the possibility of molecular architectural design in all three dimensions.

Theoretical studies of the optical properties of absorbing multilayers require allowance for the anisotropy of the refraction and absorption of light; for monoaxial structures (with an isolated *z* axis), such studies have been carried out[74,75]. For three-dimensional structures, it is necessary to employ the mathematical apparatus of the theory of crystal optics.

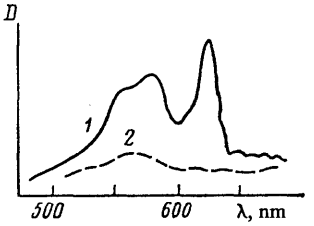


Figure 16. The dichroism of the dye (XIV) on the cleavage plane of crystalline gypsum; the polarisation vector is parallel (curve *1*) and perpendicular (curve *2*) to the *a* axis[33].

5. Spectroscopic Characteristics

Depending on the concentration of the dye in the monolayer of the surface-active substance, the type of packing of the chromophores in the monolayer, and the presence or absence of an influence of the neighbouring monolayers, the absorption and fluorescence spectra of the dye undergo significant changes, which are due primarily to the formation of different associated species. Fig.17 illustrates the transformation of the absorption spectrum of the dye (XVIII) with increase of its molar concentration in the monolayer of cadmium arachidate from 1:100 to 1:1, The increase of the intensity of the absorption band of the dimers (460 nm), associated with the suppression of the absorption band of the monomer, is clearly seen.

A further increase in the concentration of the dye (for example, its employment in a pure form without admixture of aliphatic acids) leads to an even more notable aggregation effect. Fig.16, for example, shows clearly a narrow absorption peak (λ = 625 nm), usually attributed to the parallel packing of the chromophores of the "brickwork" type (J-aggregate). The vibrations of the electronic oscillators of individual molecules take place in phase and are added together ensuring an intense absorption of light in a narrow spectral range.

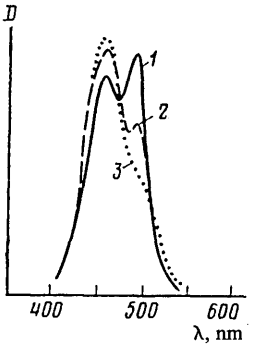


Figure 17. The equilibrium between the monomers (λ_{max} = 490 nm) and dimers (λ_{max} = 460 nm) of the dye (XVIII) in a monolayer of cadmium arachidate for different molar ratios of the two components: 1) 1:100; 2) 1:10; 3) 1:1.[2]

The spectroscopic properties of a dye in a monolayer are influenced by the molecule of the same or another dye in a neighbouring monolayer. The extent of this influence is determined by the distance between the corresponding chromophores. For example, if one monolayer contains the dye (VII) and another the dye (XVIII), mentioned above, and their chromophores are separated by alkyl chains, then the overall absorption spectrum of the two dyes constitutes a simple superposition of their individual spectra. On the other hand, if the chromophores of these two dyes are in contact, the overall spectrum is appreciably modified, i.e. exciton effects arise[2]. In a number of instances the fluorescence spectra of such systems with chromophores in contact show broad long-wavelength bands due to the formation of excited dimers (excimers). The effects of the interaction of the molecules (particularly those of chlorophyll) in neighbouring monolayers are easily observed also in the infrared absorption spectra[76].

An interesting example of the dependence of the absorption spectrum of Langmuir multilayers on the polarisation of light is presented in Fig.15*a*. For light with the polarisation e_1, the absorption maximum is displaced towards shorter wavelengths compared with the maximum for the polarisation e_2. This is caused, on one hand, by the interaction of static molecular dipoles with one another and, on the other hand, by the deviations from the ideal orientation of the molecules of the azo-dye in the multilayer. Then the light with the polarisation e_1 "selects" the molecules oriented on average along the normal to the layer and that with the polarisation e_2 "selects" molecules which have deviated from the ideal orientation. If the static dipole moments of the ground (μ_g) and excited (μ_e) states of the dye molecule are different [for the azo-dye (XV) their difference is $\Delta\mu = \mu_e - \mu_g \cong 3$ D[77]], then the spectral shift is proportional to the product $\mu_g\Delta\mu$ and depends on the angular scatter of the molecular orientations[73].

6. The Transmission of Excitation Energy and the "Photon Funnel"

One of the most impressive achievements of molecular architectural design has been the elucidation of the mechanisms for the transmission of excitation energy from one molecule (of a sensitiser or energy donor) to another (energy acceptor). This question has a long history and is extremely important in practice, because the development of methods for the sensitisation of photographic and other photosensitive materials depends on its solution.

The simplest mechanism for the transfer of energy from one molecule, excited by a light quantum, to another, unexcited molecule involves radiative transfer in which the acceptor molecule simply absorbs the light emitted by the luminescent donor molecule. In thin Langmuir films this mechanism hardly operates because of the weak absorption of light by one or several dye monolayers. The second possible mechanism involves Förster energy transfer; this mechanism operates when the acceptor molecule is at a short distance from the donor molecule. It is known that in the nearest region, i.e. at distances $R \ll \lambda$, the electric field of the emitting dipole decreases in proportion to R^{-3}. In this region the electric wave has not yet been formed, although the energy of the alternating electric field can be transmitted to a neighbouring oscillator. Such energy transfer has come to be regarded as non-radiative, although the probability of this process is proportional to the degree of overlap of the luminescence band of the donor and the absorption band of the acceptor. The third, also non-radiative, mechanism of energy transfer with the aid of exciton excitations is possible only for close packing of the donor and acceptor molecules.

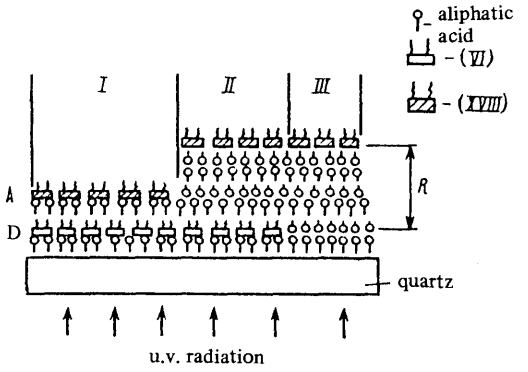


Figure 18. The scheme of Kuhn's experiment[2] designed to elucidate the mechanism of the transmission of excitation energy from the molecules of the sensitiser D to those of the acceptor A.

Fig.18 illustrates the scheme of Kuhn's experiment[2] designed to elucidate the mechanism of energy transfer between monolayers. A monolayer of sensitiser molecules D is deposited on a transparent quartz support (the insulating monolayer of aliphatic acids plays an auxiliary role). The oxacyanine dye (VI) mixed with cadmium arachidate was used for the molecules D. The monolayer of acceptor molecules A [the dye (XVIII) mixed with cadmium arachidate] is separated from the sensitiser layer by several cadmium arachidate monolayers. The number of these monolayers can be varied at will. Illumination of the sensitiser through the support by ultraviolet light leads to the following picture. On the right-hand side (III), where there is no sensitiser, the field of observation is dark, since the acceptors do not absorb the ultraviolet light. In region II, where the acceptor molecules are at a long distance from the monolayer of D molecules, the blue fluorescence from sensitiser molecules absorbing ultraviolet light, is observed. The molecules of the acceptor A absorb little of the fluorescence of the donor D, which is itself weak, and this hardly alters the spectral composition of the latter. In region I the acceptor molecules fluoresce intensely in the yellow part of the spectrum. They clearly receive energy from the molecules of the donor D by a non-radiative process. By altering the number of monolayers separating the D and A monolayers and by measuring the fluorescence intensity of the acceptor A, it is possible to test the theory developed for the Förster mechanism. Fig.19 illustrates the corresponding curve (curve *1*)[3]. Evidently the resonance non-radiative energy transfer is effective over distances of ~ 50–100 Å and less.

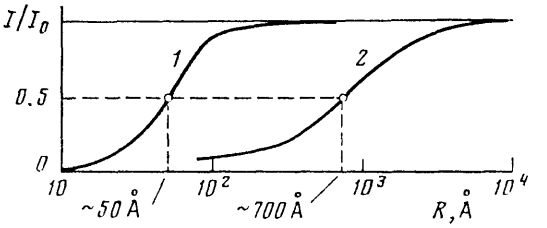


Figure 19. Dependence of the fluorescence intensity of the acceptor molecules on the distance R between the acceptor monolayer and the sensitiser monolayer (in Fig.18) (curve *1*) and between the acceptor molecules within a single monolayer (in Fig.20) (curve *2*).

Extensive studies on the mechanism of the excitation energy transfer through dielectric monolayers, carried out by Kuhn et al.[2] and Drexhage[3], confirm the validity of the Förster mechanism not only for dielectric dipolar oscillators but also for emitters of the type of a magnetic dipole and an electric quadrupole. The non-radiative energy transfer can occur from both singlet and triplet states of the sensitiser[78].

An absolutely different situation obtains when the acceptor molecule, with a structure similar to that of the donor molecule, is introduced into a continuous monolayer formed by the donor molecules. As already stated, the close packed chromophores (in the given instance of the donor molecules) form ordered assemblies which collectively absorb and emit light within narrow spectral ranges (*J*-aggregates). The acceptor molecules introduced into the same monolayer effectively absorb the energy of the *J*-aggregates, transforming it into the emission of their intrinsic luminescence. Fig.20 illustrates the fluorescence spectrum of a mixed monolayer in which there is only one acceptor molecule (trimethine and pentamethine surface-active cyanine dyes[79]) for each 250 sensitiser molecules. Despite the sharp difference between the donor and acceptor concentrations, the fluorescence intensity from the long-wavelength band (acceptor band) is almost the same, while at liquid nitrogen temperature it is

actually higher than from the short-wavelength band of the donor. This demonstrates that the energy of the light absorbed by a large number of donor molecules is concentrated at a single acceptor molecule, i.e. the principle of the "photon funnel" is realised.

Exactly the same experiment has been carried out recently with the dyes (VI) and (VII) as the donor and acceptor respectively[5]; the concentration of the molecules of the dye (VII) in the monolayer of the dye (VI) was varied. The fluorescence intensity of the acceptor molecules was plotted against the average distances between them (see Fig.20 and curve *2* in Fig.19). Fig.19 shows that in this case the characteristic distance from which the acceptor collects energy is ~ 700 Å and the number of donor molecules forming the "photon funnel" is 5×10^4. This figure agreed with the exciton mechanism of energy transfer: during its lifetime (~ 10^{-9} s), the exciton executes ~ 10^4 jumps from molecule to molecule and gives up its energy to the acceptor molecule if the latter is encountered in its path[6].

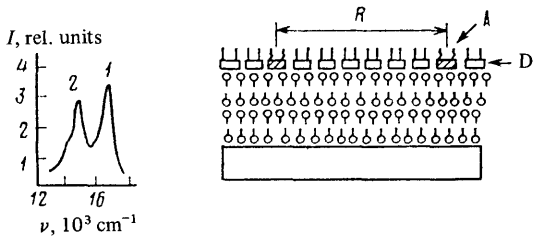


Figure 20. The fluorescence spectrum of a mixed monolayer of donor and acceptor molecules: 1) spectral maximum of the donor; 2) spectral maximum of the acceptor.

Experiments in recent years have shown that the principle of the "photon funnel" discussed above plays a key role in the mechanism of photosynthesis, where one trapping molecule collects the energy from ~ 300 chlorophyll molecules[6].

V. EFFECTS DUE TO "SPONTANEOUS" POLARISATION

1. "Spontaneous" Polarisation#

A completely new trend in molecular architectural design is the creation of asymmetric structures without an inversion centre. A whole series of new properties appear in such structures. We have already spoken of the idea of creating a molecular rectifier; in the next section we shall discuss vectorial electron transfer under the influence of light and now we shall consider the question of the presence of a permanent dipole moment per unit volume of a monolayer or multilayer, i.e. "spontaneous" polarisation *P*.

Turning to Fig.5, we may note that, in the presence of a longitudinal molecular dipole moment μ in the surface-active molecules, layers of type *X* and *Z* should have an overall dipole moment $P = \mu n$, where $n = N_A \rho / M$ is the number of molecules per unit volume (ρ is the density and *M* the molecular weight). In layers of type *Y*, where the overall dipole moments of the monolayers are compensated, $P = 0$. The numerical value of the polarisation for layers of types *X* and *Z* is $P \cong 10^6$ C cm^{-2} for $\mu = 6$ D and $M = 400$ g mol^{-1}.[23] In the experimental determination of the "spontaneous" polarisation, it is necessary to overcome at least two difficulties. Firstly, it is necessary to obtain layers of type *X* or *Z*, which cannot be always achieved; in particular, the molecules of aliphatic acids tend to be arranged in layers of type *Y* whatever the method of deposition. Secondly, the "spontaneous" polarisation, equal to the surface charge density on the multilayer, is usually compensated by the free charges due to the conductivity of the specimen or other leakages. It is therefore possible to measure experimentally not the absolute value of *P* but the changes in it, for example, when the temperature (pyro-effect) or pressure (piezo-effect) is altered. The value of *P* can also be calculated in terms of the molecular dipole, provided that there is an independent method of checking the state of orientation of these dipoles (for example, on the basis of the linear Stark effect—see below). The estimate of *P* quoted above has been obtained[23] by the last method for the azo-compound (XV).

2. The Pyro- and Piezo-Effects

The pyroelectric effect was first observed on *X*- and *Z*-type multilayers of the azo-compounds (XV) and substituted benzenes (XIX)[80]. In order to observe the effect, multilayers consisting of 10–100 monolayers were illuminated by pulses from a laser at a wavelength $\lambda = 1.06$ μm. Light was absorbed in a semi-transparent aluminium electrode and heated the multilayer. A potential pulse then arose on the electrodes, characterised by the pyro-coefficient $\gamma = dP/dT$. The sign of this pulse was the opposite of that for multilayers of the *X* and *Z* types; on layers of the *Y* type, the pyrosignal was not observed. This fact and also the kinetics of the increase and fall of the signal made it possible to establish its pyroelectric nature. The calculated value of γ for a 100-layer structure of the *X* type [compound (XV)] with $R = SO_2NH_2$ is 3×10^{-10} C cm^{-2} K^{-1}, which is lower approximately by an order of magnitude than the pyro-coefficient of film pyroelectrics[114].

The piezoelectric effect can be observed by a very clear procedure using the repeated reflections of a sound wave in a glass support on which a multilayer of the *X* or *Z* type has been deposited[23]. This wave can be obtained by the optoacoustic method, provided that the glass (for example, an SZS-21 light filter) absorbs the pulse of the laser emission at a wavelength $\lambda = 1.06$ μm. The resulting acoustic wave and its frequent repetitions (echo) excite in the multilayer the piezoeffect pulses, which can be observed on an oscilloscope screen using sputtered metallic electrodes, one of which has been deposited on glass (under the layer) and the other on the multilayer. The signs of the piezo-effect are different for layers of the *X* and *Z* types; the effect has not been observed on layers of the *Y* type.

3. The Linear Stark Effect

The observation of the spectral shift (linear in terms of the field) of the electronic absorption band in an external electric field constitutes a powerful quantitative method for the investigation of the polar structures of Langmuir films.

More precisely, we are dealing with macroscopic polarisation due to the process involved in the preparation of the multilayers.

Suppose that a molecule has a dipole moment μ_e in the excited state which does not coincide with the dipole moment in the ground state μ_g, i.e. $\Delta\mu = \mu_e - \mu_g \neq 0$. The ground and excited energy levels in an electric field **E** are then displaced by $\mu_g\mathbf{E}$ and $\mu_e\mathbf{E}$ respectively and the shift of the absorption band is $\Delta h\nu = (\mu_e - \mu_g)E$ (for simplicity it is assumed that the field is directed along the μ_e, μ_g, and $\Delta\mu$ vectors). The direction of the spectral shift is determined by the sign of $\Delta\mu$. If the molecular dipoles in the film lie in one direction, the shift of the absorption band of the film corresponds to the shift of the absorption band of the molecule. Otherwise, the spectral shifts towards long-wavelengths and short-wavelengths are averaged out owing to the scatter of the angles between the directions of the vectors **E** and $\Delta\mu$. The spectral shift of the band in an electric field implies an alteration of the optical transmittance at the specified wavelength. The amplitude of the relative change in the transmittance $\Delta T/T$ is proportional to $\langle\cos\theta\rangle$, where θ is the angle between the vectors $\Delta\mu$ and **E**. In the experimental observation of the linear Stark effect (Fig.21), the electric field vector is usually directed along the normal to the film. If the direction of the vector $\Delta\mu$ coincides with the molecular axis, as happens for the azo-compounds (XV), then the angle θ is the angle of deviation of the molecular axis from the normal. Thus the amplitude $\Delta T/T$ is a measure of the approach of the molecules to the ideal orientation (in which $\langle\cos\theta\rangle = 1$).

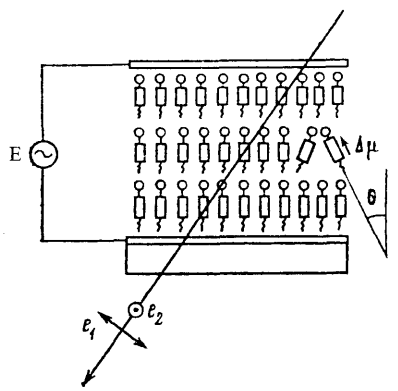


Figure 21. Measurement of the linear Stark effect for a multilayer structure. The molecules of compound (XV) have a chromophoric azo-system (rectangles) and an acceptor group R (circles). There is a transparent SnO_2 electrode on a quartz support and a semitransparent aluminium electrode on top of the multilayer.

Fig.21 illustrates the experimental arrangement designed to observe the linear Stark effect in a multilayer of the *Z* type formed by the azo-compounds (XV)[23]. The polarisation of the light can be of any kind provided that the molecules are scattered at angles θ; otherwise light with the usual polarisation is not absorbed. The changes in the optical transmittance of the film following the application of an external field are illustrated in Fig.22. The $\Delta T/T$ spectrum has the same form as the $dD/d\lambda$ spectrum if one disregards the slight ($\Delta\lambda \cong 10$ nm) mutual shift of these curves due to the different forms of the averaging of the optical and electro-optical contributions by the individual molecules[81]. The value of $\langle\cos\theta\rangle$ is calculated from the $\Delta T/T$ amplitude.

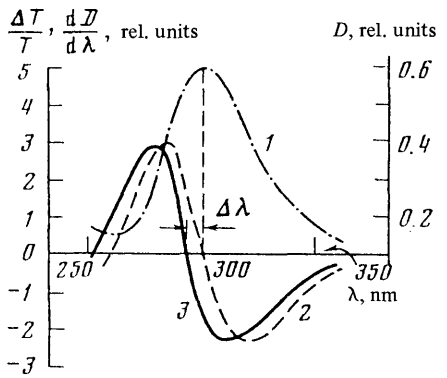


Figure 22. Curves representing the optical density *D* (curve *1*), its first derivative with respect to the wavelength $dD/d\lambda$ (curve *2*), and the $\Delta T/T$ Stark effect signal (curve *3*) for an *X*-type multilayer of compound (XV) with R = $SO_2N.(C_2H_5)_2$.[81]

The $\Delta T/T$ Stark signals for films of the *X* and *Z* types have opposite signs; on *Y* layers, the $\Delta T/T$ amplitude is approximately 30 times lower and is due to the incomplete compensation of the dipole moments of the neighbouring monolayers[23].

We may note that the combination of the dichroism[73] and the linear[81] and quadratic[82] Stark effect methods makes it possible to estimate not only $\langle\cos\theta\rangle$ for Langmuir films but also the next three terms in the expansion of the orientation distribution function of the molecules ($\langle\cos^2\theta\rangle$, $\langle\cos^3\theta\rangle$, and $\langle\cos^4\theta\rangle$)[82]. Measurements of the linear Stark effect together with the pyro- and piezo-effects convincingly demonstrate the polar structure of films of the *X* and *Z* types.

4. Generation of the Second Harmonic of the Light and the Photogalvanic Effect

The polar structure of layers of the *X* and *Z* types must lead to a further two effects which have not so far been observed experimentally. Firstly, symmetry considerations allow in the given instance the generation of the second harmonic of the light via a dipole mechanism (we are dealing with the doubling of the frequency of a powerful light beam). Secondly, intramolecular charge transfer from the donor substituent to the acceptor (for example in azo-compounds) should lead to a potential difference between the electrodes of the multistructure illustrated in Fig.21 when the latter is illuminated (the photogalvanic effect). This potential difference should be proportional to $\Delta\mu$ and to the number of molecules excited by the light with wavelength corresponding to the intramolecular charge transfer band, which is in its turn proportional to the light intensity and to the lifetime of the molecules in the excited state.

VI. PHOTOELECTRIC AND PHOTOCHEMICAL PROPERTIES

1. Electron Transfer

The study of the photoelectric and photochemical properties of artificial multimolecular structures is perhaps the most important trend in molecular architectural design. This concerns the modelling of the processes involved in photosynthesis, the photolysis of water, the creation of solar energy converters, etc. The key factor in all these problems is the achievement of a directed (vectorial) electron transfer from one molecule to another.

The vectorial electron transfer under the influence of a light quantum is modelled by a two-layer structure formed by a monolayer of electron-donating dye molecules and the monolayer of electron accepting molecules (Fig.23)[6]. The thiacyanine dye (VII) can serve as the donor and the bipyridylium salt (XX) (viologen) can serve as the acceptor. When this two-layer system is illuminated by light at wavelengths corresponding to the absorption band of the donor molecules, the excited electron, raised to the highest level of the donor molecule, can tunnel through the dielectric layer to the highest unoccupied level of the acceptor molecule. This transfer can be observed by the quenching of the fluorescence of the donor. The transmission of energy via the mechanisms discussed in the previous section is ruled out in this instance, since compound (XX) has no absorption bands in the spectral region of the fluorescence of the dye (VII). The intensity of this fluorescence depends very markedly on the distance between the chromophoric chains of the donor and acceptor molecules. Thus in case *1* (Fig.23) the fluorescence is quenched completely, in case *2* it diminishes approximately by a factor of two, and in case *3* it hardly changes.

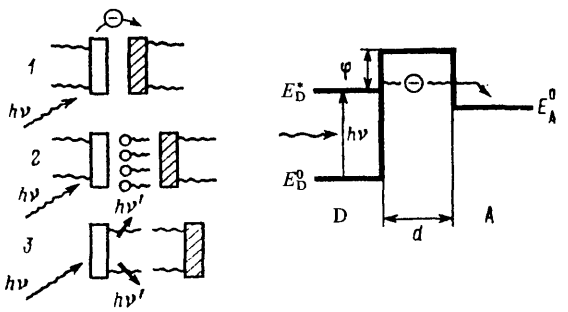


Figure 23. Electron transfer from the photoexcited state of the donor molecule to the highest unoccupied orbital of the acceptor molecule. Open rectangles—electron donor molecules; filled rectangles—electron acceptor molecules; ν' = fluorescence frequencies; in case (2) there is an intervening layer of aliphatic acid molecules[6].

Such a pronounced dependence of the fluorescence intensity on the thickness of the dielectric layer is consistent with the tunnel mechanism of electron transfer through the potential barrier. Experiments in which the width of the tunnel barrier, i.e. the thickness of the aliphatic monolayer, illustrated in scheme *2* (Fig.23), was altered by replacing one aliphatic acid homologue by another (the number of carbon atoms increased from 14 to 22) served as a quantitative confirmation of this postulate[5,6]. The fluorescence intensity diminished exponentially in conformity with the theory of tunnel currents (Fig.24).

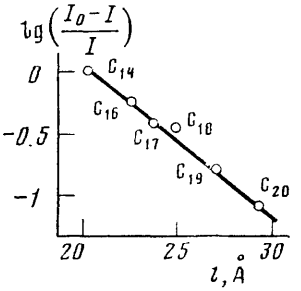


Figure 24. The quenching of the fluorescence intensity of the donor I as a function of the thickness of the tunnel barrier; I_0 = intensity in the absence of a layer of acceptor molecules[6].

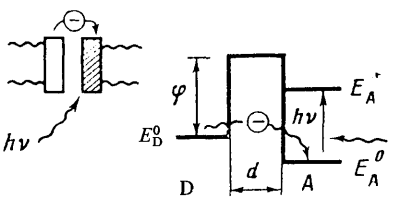


Figure 25. Electron transfer on photoexcitation of the acceptor molecule. Open rectangle—electron donor molecule; filled rectangle—electron acceptor molecule[6].

The degree of quenching of the donor fluorescence depends not only on the width of the barrier but also on the relative positions of the energy levels of the donor and acceptor. In particular, a decrease in the ionisation potential of the donor increases the probability of the electron tunnelling and enhances the quenching effect[83]. The quenching intensifies also on formation of *J*-aggregates by the donor molecules[84].

A second example of photoinduced electron transfer is illustrated in Fig.25. In this case light excites the acceptor molecule and the electron passes from the highest occupied orbital of the donor molecule to a liberated site in the lowest level of the acceptor. Examples of such electron-donating and electron-accepting molecules are provided by compounds (XXI) and (XXII) respectively. In this case the electron transfer from compound (XXI) to (XXII) is monitored by observing the quenching of the fluorescence of the dye (XXII)[2,6].

2. The Electron "Pump"

The photoinduced vectorial electron transfer from the donor to the acceptor molecule, illustrated in Fig.23, is accompanied by the reverse (dark) process, involving the

tunnelling of the electron through the barrier from A to D. However, the two schemes can be combined (Figs.23 and 25) by exciting with light the dye which serves as an electron acceptor in relation to one molecule and at the same time as an electron donor in relation to another. Such a scheme is illustrated in Fig.26. The molecule of the surface-active compound (XXIII) can be conveniently employed as the photosensitive species. The photoinduced electron transfer to the acceptor—the distearylbipyridylium salt (XX)—takes place when a monolayer of these molecules is illuminated. The lost electron is replaced by an electron from the dye-source [the leuco-form of the dye Stearylene Blue (XXIV)].

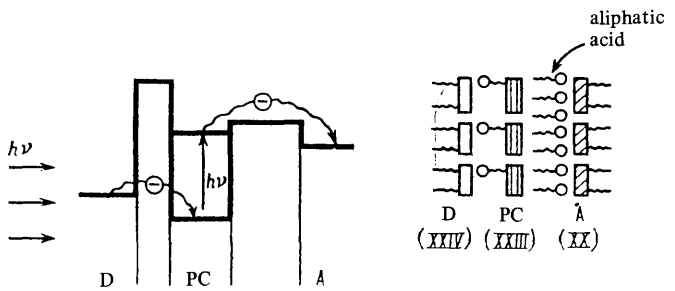


Figure 26. Schematic illustration of the "electron pump"; D = electron source molecule; PC = photocatalyst; A = electron acceptor molecule.

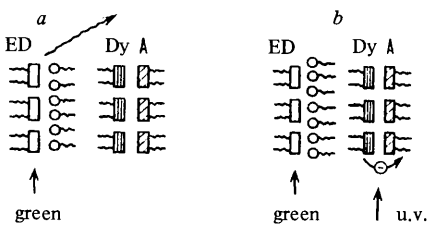


Figure 27. Illustration of the combined effect of the electron phototransfer from the dye Dy to the acceptor A and of the excitation energy transfer from the energy donor ED to A.

Thus the multistructure illustrated in Fig.26 effects a two-stage electron transfer from the source molecule S to the acceptor molecule; the intervening layer plays the role of the photocatalyst PC. As a result of such transfer, the energy of the electron increases. Consequently this structure effects the pumping of electrons from lower energy levels to higher levels, i.e. plays the role of a molecular "pump" for electrons.

The operation of this "pump" can in principle be monitored by the appearance of the oxidised (blue) form of the dye (XXIV) or the reduced form (also blue) of viologen (XX). However, this is difficult to achieve experimentally. A more effective method of detecting the viologen radical involves the observation of the quenching of the fluorescence of special molecules (energy donors) added to the multistructure and chosen in such a way that their fluorescence band coincides with the absorption band of the viologen radical. Then, in the absence of electron transfer in the dye–acceptor (viologen) pair (Fig.27*a*), the energy donor (ED) fluoresces under the influence of visible light, for example, in the red region. Illumination of the dye Dy with ultraviolet light leads to electron transfer from the dye molecule to the acceptor, whereupon viologen is converted into a radical which also absorbs light in the red part of the spectrum. The non-radiative (Förster) mechanism of energy transfer from ED to A begins to operate, which is indeed observed experimentally as the quenching of the red fluorescence of the energy donor[5].

3. Photoconductivity and Photo-e.m.f.

The vectorial phototransfer of an electron can be investigated also by a purely electrical method involving the measurement of the photocurrent in an external circuit for different polarities of the field applied to the specimen or the photo-e.m.f. induced in the electrodes of the specimen.

A fairly large number of studies have been made of the photoconductivity of Langmuir films sensitised by dyes. The physical mechanism of the primary process involving the appearance of a photoelectron in the specimen has been considered[85] in relation to a multilayer structure into which a monolayer containing molecules of quinquethienyl (X), whose electronic oscillators are perpendicular to the plane of the layers (Fig.28), was introduced. The monolayer of quinquethienyl is located among the layers of cadmium arachidate and its position (more precisely its coordinate x) can be varied at will. A potential U, which "inclines" the potential energy diagram for the system, is applied between the mercury and aluminium electrodes. Under the influence of light, electrons pass from the highest occupied orbital of the quinquethienyl molecule to the lowest unoccupied orbital; hence the electrons tunnel across the barrier (or pass through it) and appear in one of the bound energy states on the surface between neighbouring cadmium arachidate monolayers (Fig.9). Next electrons move to the positive electrode via the jump mechanism considered in Section III. The first stage in overcoming the barrier limits the photocurrent. If the ionisation potential of quinquethienyl is ϕ_0 before the application of the external electric field, then it is clear from simple geometrical considerations that in the electric field it falls to $\phi = \phi_0 - eU(L/2d)$, where L is the length of the molecules of compound (X). The current in the external circuit should be proportional to the probability of the escape of electrons from the quinquethienyl molecules to the positive electrode [i.e. to the factor $\exp(-\phi/kT)$] and the time taken to traverse the distance x. Indeed the exponential increase of the current with increase in the potential and the linear dependence on the position of the layer of compound (X) in the multistructure have been observed experimentally[85]. Other results[86] also confirm the model under consideration.

In structures of the type illustrated in Fig.28 it is possible to observe not only a transverse (across the multilayer) but also a longitudinal (in the plane of the layers) component of the photoconductivity. This can be done with the aid of photosensitisers of a new type incorporating the rhodanine fragment (XXV)[87]. The photoconductivity of the longitudinal type exceeds by 2–3 orders of magnitude the transverse component and its temperature variation is of a different type, which agrees with the jump model of the transverse conduction considered previously and the non-active mechanism of the longitudinal conduction[8].

The transverse photoconductivity can be greatly increased by employing, instead of the simple sensitiser shown in Fig.28, a more complex, "photosynthetic" system[88] consisting of monolayers of an electron acceptor and donor and a "molecular conductor" between them[31,54]. Such "construction" of the sensitiser makes it possible to increase the probability of its photoionisation. The corresponding multistructure and energy diagram are shown in Fig.29.

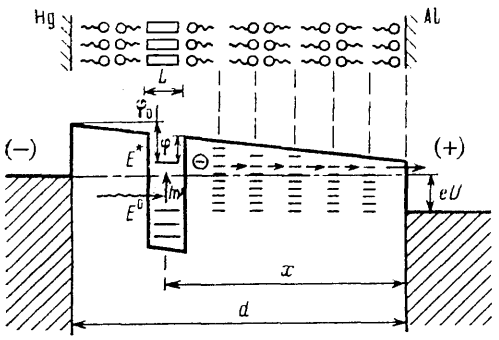


Figure 28. Model elucidating the mechanism of photoconduction in a cadmium arachidate multilayer sensitised by a monolayer of quinquethienyl (X)[85].

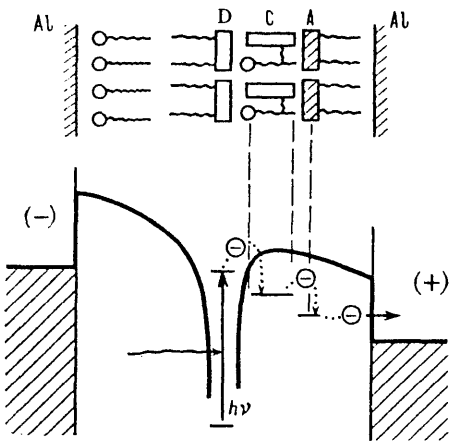


Figure 29. Model elucidating the electronic transitions in the donor D—molecular-conductor C—acceptor A—positive electrode system[54].

In the example given, the rectangular potential well for the electron-donating dye [the indocarbocyanine dye (XXVI)] has been replaced by the more realistic Coulombic potential. The tunnel or thermoactivated electron transfer from the photoexcited state of the donor to the free orbital of the acceptor (XX) is facilitated by the presence of the "molecular conductor" C containing the conjugated chain of the azochromophore of compound (XII). The presence of this chain decreases the width of the potential barrier which must be overcome by the electron tending to enter the acceptor and then the electrode. At any rate, the absence of the molecules of C decreases the photocurrent by an order of magnitude[54]. The change in the polarity of the applied potential results in an appreciable difference in the photocurrent. Since the electrodes are the same in the given instance, this partial "rectification" of the current is caused exclusively by the asymmetry of the "photosynthetic" unit.

The artificially created asymmetry of the multilayer is a necessary attribute required to obtain a photoelectromotive force at the electrodes when the latter are illuminated. Artificial membranes immersed in the solution were used previously to obtain a photo-e.m.f., the opposite surface of the membrane being in contact with solutions of different types. Photo-e.m.f.'s of the order of fractions of a volt were achieved in this way following the illumination of membranes by light from standard light sources[89,90]. Approximately the same photo-e.m.f.'s have been observed also on asymmetric Langmuir multilayers[54,91]. Here an additional factor promoting an increase of the photo-e.m.f. is the use of asymmetric electrodes made, for example, of metals having different electron work functions[54] or using oxide films, the photo-e.m.f.'s reaching several volts in the latter case[92].

4. Photochemical Aspects

There exist fairly numerous publications devoted to the study of the photochemical reactions in monolayers on the surface of water and also in Langmuir multistructures. Their detailed consideration is outside the framework of this review. We shall only note some of the trends which are closest to the idea of molecular architectural design. In particular, photochromic compounds are of special interest for the creation of artificial structures modelling optical memory devices. The surface potential and the area per molecule in monolayers of surface-active photochromic compounds change under the influence of illumination, which can be measured with the aid of the Wilhelmy balance[93,94].

Extensive studies on various photochemical reactions in Langmuir monolayers and multilayers have been carried out in Whitten's laboratory (see, for example, Refs.95—98). The formation of photodimers and excimers, photochemical oxidation and reduction processes (particularly those involving porphyrins), the photoisomerisation of olefins, the photochemical reactions of ketones and surface-active styrene derivatives, and other reactions[12] have been investigated. It was found that the structure of the monolayer has a decisive influence in many instances not only on the rate of reaction but also on the type of final products. As a rule, products whose structure is compatible with the symmetry of their environment are preferred. It has been noted[97,99] that compounds bound in the Langmuir matrix can serve as more effective reagents and also as catalysts of chemical reactions than the compounds in an isotropic solution.

Special mention should be made of polymerisation reactions in solid Langmuir films. Their investigation was begun comparatively recently[100], but important practical results for a whole series of different compounds have already been obtained[10-12]. Ultraviolet radiation, electron beams, and γ-radiation (in particular that from a ^{60}Co source) have been used to initiate polymerisation in multilayers.

The polymerisation of diacetylene derivatives (V) can serve as an example. Under the influence of ultraviolet light, the Langmuir monolayers of compound (V) deposited on a quartz or silicon support react as follows[101]:

$$\mathrm{R{-}C{\equiv}C{-}C{\equiv}C{-}R' \rightarrow \cdots = [=C{-}C{\equiv}C{-}\overset{\displaystyle R'}{\overset{|}{C}}{=}]= \cdots}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \mathrm{R}$$

The structure of the monolayer, determined by X-ray diffraction, does not change significantly under these conditions. In general the polymerisation process occurring within the plane of a single monolayer does not as a rule involve the molecules of another layer, which extends the scope of molecular architectural design, permitting the successive deposition of polymer layers made up of different compounds.

An interesting example of a compound which polymerises under the influence of an electron beam is ω-tricosenoic acid. The molecules of this compound in the Langmuir monolayer are oriented at right angles to the support and their cross-linking at the site of the rupture of the unsaturated bond takes place within the plane of the monolayer. The stable multilayers used as electron resists are obtained by this method[102].

A survey of studies of polymerisation in monolayers and of the preparation of monolayers and multilayers directly with the aid of polymer molecules has been published recently[12].

VII. PROBLEMS OF MOLECULAR ARCHITECTURAL DESIGN: REALITY AND PROSPECTS

Molecular architectural design, i.e. the creation of complex molecular assemblies with a predetermined architecture, leads to boundless possibilities for their applications in a wide variety of branches of science and engineering if one disregards technical difficulties. Only some of them are illustrated in the scheme below but the advances in molecular architectural design have already been significant; the corresponding literature sources are indicated in the subsection on technical applications.

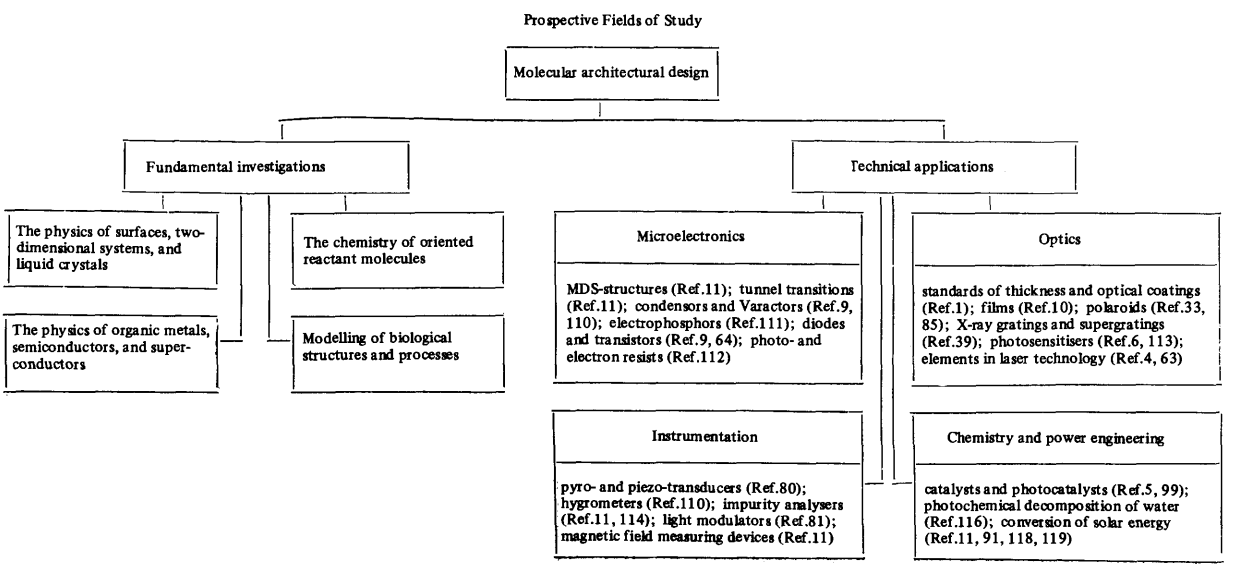
1. Fundamental Investigations

Evidently a monolayer resting on the surface of water or transferred onto a solid support can serve as an excellent model of a two-dimensional condensed medium. Studies of the structures of such monolayers have become particularly urgent now that impressive advances have been made in the theory of phase transitions in three-dimensional bodies and the general development of statistical physics of condensed media is directed towards the study of media with a reduced dimensionality. A number of investigations[27,30,122] can serve as examples. The study of the surfaces of solids and liquids also belongs to this field.

Problems concerning the structural organisation of a single monolayer and the correlations in the packing of molecules in neighbouring monolayers, which are in contact with one another, have a direct bearing on the physics of smectic liquid crystals[103] and can be solved with the aid of model systems such as Langmuir layers. On the other hand, a number of ideas in the physics of liquid crystals, concerned, for example, with the explanation of the mechanism of ferroelectricity, can be successfully transferred to the physics of membranes and artificial monolayers and multilayers[104].

In the future molecular architectural design will become a standard procedure for the investigation of a wide variety of processes occurring in organic solids. We have already spoken of the advances in the spectroscopy of complex organic molecules and various associated species, about the mechanisms of the transfer of excitation energy, etc. (Section IV). With the aid of Langmuir films, it is possible to investigate also other exciton processes, in particular, the interaction of excitons with the surface of a crystal, with admixtures, or with metallic electrodes[7,105,106].

It is known that the relative positions of the donor and acceptor fragments of molecules (in the form of stacks, columns, etc.) plays a decisive role in the exciton mechanism of the superconduction in organic crystals. Such structures can be built up in principle on the basis of Langmuir films. Experiments with anthracene derivatives indicate a "stacked" structure of multilayers, leading to a pronounced anisotropy of the electrical conductivity[34]. A similar structure is also characteristic for example, of quinquethienyl layers[85]. Donor–acceptor two-layer systems, formed, for example, by the surface-active analogues of compounds such as tetrathiofulvalene and tetracyanoquinodimethane (TTF–TCNQ complexes), as well as other compounds of this type, which do not form crystals with a suitable structure[9], are of undoubted interest for the physics of organic metals and superconductors.



There is no necessity to mention that chemical and physicochemical reactions involving reactants whose molecules are rigorously oriented in space provide the experimenter with a greater "degree or freedom" than do experiments with isotropic solutions. Clearly in the oriented state it is possible to involve new molecular fragments in the reaction. For such chemical reactions, one can use various boundaries (between the monolayer and the support, between the monolayer and the external environment, and also the boundary between the monolayers)[99]. As already stated, it is thereby possible to alter not only the rates of the reactions but also their products (an example is provided by the formation of a silver mirror at the interface between a monolayer and water[107]).

Molecular architectural design is perhaps of greatest interest for the modelling of various biological processes, in particular the primary stages of photosynthesis. The attempts to model the molecular antenna (or "photon funnel"[5,79]) and also the fundamental photocatalytic electron transfer from a donor to an acceptor[5,6,108] and the replication of information at the molecular level[7] can be regarded as entirely successful. Other model biological studies, including the modelling of the self-organisation of matter[109], are apparently tasks for the immediate future.

2. Technical Applications

The incorporation of molecular architectural design in technology proceeds mainly via four pathways (Fig.30). Microelectronics, where Langmuir films can already be used in commercially produced instruments, can apparently be placed in the first place. This applies primarily to the dielectric layers in metal–dielectric–semiconductor structures, for example, field effect transistors, where the current flowing through the semiconductor is controlled by the electric potential of the metallic electrode separated from the semiconductor by a thin dielectric layer. In field effect transistors based on silicon, the natural oxide layer plays the role of the dielectric. Other semiconductors (for example, InP or CdTe) do not have an oxide film and an additional layer of dielectric with a high electrical strength is essential. Langmuir multilayers, for example, those based on polymerised diacetylenes (a layer with a calibrated thickness and consisting of several tens of monolayers is usually employed) are used as layers of this kind[11].

Ultrathin Langmuir multilayers (with a thickness equivalent to 1–4 monolayers) are also used as tunnel junctions in "cold cathodes" employing the properties of the contact between a photoconductor and a metal. A Schottky potential barrier is usually formed on such contacts. Under the influence of light, a photo-e.m.f. is generated at the site of contact between the semiconductor and the metal and the structure itself becomes an effective converter of light energy into electrical energy. The use of an additional (tunnel) dielectric layer between the metal and the semiconductor improves the efficiency of the conversion of light energy into electrical energy. Thus the efficiency of the "cold cathode" on *n*-type cadmium telluride increases by a factor of 1.4 when two monolayers of the substituted anthracene (VIII) are deposited on the semiconductor[11].

By virtue of their high electrical strength and the possibility of the preparation of films with a rigorously specified and very small thickness, Langmuir monolayers and multilayers are extremely convenient dielectrics for the preparation of high capacitance condensers. The capacitance reaches 0.1 $\mu F\ cm^{-2}$ for the field strength corresponding to breakdown, $\sim 3 \times 10^6\ V\ cm^{-1}$.[110] Condensers whose capacitance is altered under the influence of an external field (Varactors) can also be prepared on the basis of Langmuir films[9].

The unusual type of molecular packing in Langmuir films makes it possible to achieve a high luminescence and electroluminescence (arising from the application of an electric field) quantum yields in them[34,111]. Electrophosphors based on Langmuir films can prove promising for the creation of electroluminescent devices for the reproduction of information (digital displays, panels, flat television screens, etc.). The formation of donor–acceptor multilayers, the employment of surface-active complexes and autocomplexes with charge transfer, and the preparation of solid multilayers based on radical-ion salts will probably lead in the near future to the creation of molecular current rectifiers and more complex transistor structures[9,64].

Quite definite advances have been made in the field of the formation with the aid of Langmuir monolayers of high-resolution photo- and X-ray-resistors.

A sensitivity to an electron beam to within $5 \times 10^{-7}\ C\ cm^{-2}$, for a contrast reaching 2 and a spatial resolution of ~ 600 Å, has been achieved recently on the basis of polymerisable ω-tricosenoic acid films[112]. It was noted that the electron resists obtained by the Langmuir Blodgett technology also exhibit a high resistance to plasma and an effective adhesion to aluminium.

The application of Langmuir films in optics (Fig.30) is based primarily on the possibility of varying their refractive indices for a rigorously specified film thickness. Hence arises the possibility of creating optical thickness standards[1], optical coatings, and interference filters as well as X-ray diffraction gratings[39] and supergratings. It has been noted[9] that X-ray gratings based on multilayers could be particularly useful in the future for the creation of lasers operating in the X-ray range.

The marked dichroism of Langmuir monolayers formed by surface-active dyes, particularly in the aggregated state[33,85,108], makes it possible to employ these structures for the creation of effective film polarizers. The selective absorption of light by dyes can be used also in the development of film layers for the isolation of specific spectral components of radiation (the selection of modes)[63], the generation of ultrashort pulses[4], etc. One may also expect that the non-linear optical properties of polar multilayers will find fairly extensive applications in the immediate future.

Langmuir films are of great interest for integrated optics. They can be used for the creation of both waveguide elements themselves and the outer plates of such devices. The technique of the preparation of multilayers makes it possible to construct the necessary refractive index profile across an integrated optical structure. A fairly high optical quality of such structures (decay of light waves smaller than 1 dB per cm of the path traversed for film thicknesses up to 5000 Å) has already been achieved[10].

The transmission of excitation energy and vectorial electron transfer can be used successfully for the sensitisation of traditional photographic materials. Experiments with silver bromide crystals have shown that AgBr is sensitised as a result of electron transfer from an excited dye monolayer[6,7]. The presence of an electrical acceptor suppresses the sensitisation effect. Specially constructed multilayers on the surface of a photosensitive crystal make it possible to achieve simultaneously the transfer of energy from one dye to another (via the "photon funnel" mechanism), which gives up an electron in its turn to the crystal[113]. This leads to an extremely effective sensitisation of the photographic process.

A new method of recording and replication of information at the molecular level, recently proposed by Kuhn[7], is of

special interest for engineering. Recording on Langmuir films can be achieved with the aid of an electron beam, which induces a photochemical process. The rerecording of information from one monolayer to another is effected by contact procedures similar to the replication of ribonucleic acid in cell chromosomes.

On the other hand, the first attempts to create pyroelectric elements on the basis of polar multilayers led to pyrocoefficients of ~ 10^{-10} C cm^{-2} K^{-1},[80] which is only an order of magnitude lower than the corresponding values for the best film pyroelectrics[114]. In view of the low dielectric constants, which increase the quality factor for pyroelectric materials, one can regard the further development of pyroelectric radiation transducers based on Langmuir multistructures as extremely promising. This applies also to piezoelectric transducers.

There is reason to believe that the linear Stark effect, observed in polar films of surface-active dyes[81], will prove useful in the development of fast acting thin-film light modulators. It has also been suggested that tunnel transitions in Langmuir monolayers be used for the creation of highly sensitive magnetic field measuring devices[11].

Instrument engineering is in acute need of highly sensitive transducers permitting the analysis of low concentrations of admixtures of various gases, water vapour, ionic impurities in solutions, etc. The development of hygrometers based on cadmium behenate multilayers with a gold film electrode permeable to water molecules has been reported[110]. The capacitance of such a structure depends on the amount of water which has diffused through the gold electrode. Selectivity with respect to various impurities can be ensured with the aid of specially constructed multilayers deposited on the open surface of a field effect transistor sensitive to extraneous impurities[115]. The multilayers can also include various biologically active molecules which ensure the selective transport of impurity molecules (for example, via the mechanism of the action of ionophores in membranes).

Reports already exist concerning the creation of instruments detecting gases such as ammonia, carbon monoxide, and hydrogen[11,111].

The possibilities of molecular architectural design in chemistry and power engineering have been assessed very optimistically. The advantages of specific synthesis on Langmuir matrices have already been pointed out. We shall now consider the results of modern studies in the conversion of solar energy into electrical energy. One of the ways of achieving such conversion is photochemical decomposition of water into oxygen and hydrogen; certain surface-active metal complexes can then be used as photocatalysts. A successful attempt at the photochemical decomposition of water with the aid of a monolayer of a ruthenium complex has been reported[116], but subsequent studies[83,117] revealed a number of fundamental difficulties. Another procedure for the conversion of energy consists in the creation of solar batteries by analogy with semiconducting p–n junctions[88]. The Schottky barriers were already mentioned above. In addition, one can employ solid Langmuir multilayers formed by electron-donating and electron-accepting compounds[54,91] as well as electrolytic cells in which the Langmuir monolayers are deposited on a solid support with an optically transparent electrode. In the former case (chlorophyll *a* combined with quinones) the efficiency of the conversion reaches hundredths per cent for a photocurrent quantum yield of the order of several tenths per cent[91]; in the second version (a layer of chlorophyll on an SnO_2 electrode) the photocurrent quantum yield can reach 12–16%.[118,119] The corresponding efficiency of the energy conversion is lower by more than an order of magnitude than the efficiency characteristic of semiconductor solar batteries. However, it is noteworthy that the Langmuir layers are very cheap and technologically convenient. The latter factor is extremely significant when one considers the necessity to "collect" solar energy from large areas. Furthermore, one can employ the principle of the "photon funnel" for the collection of light energy with the aid of a combination of dyes in an energy converter incorporating an electrolytic cell. This should yield an appreciable gain in the efficiency of the conversion[120,121].

In conclusion of the review we emphasise that molecular architectural design is now entering the period of its vigorous expansion and we are justified in expecting from this new field new scientific discoveries and important practical applications.

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Organic Metals and Superconductors Based on Tetrathiofulvalene Derivatives

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The latest advances in the synthesis and research into organic metals based on various heterocyclic systems are examined. The influence of the structure of the organic donor and of the size and geometry of the anions on the electrophysical properties of compounds of this series and the conditions governing the appearance of their superconductivity are discussed in relation to compounds of the class of tetrathiofulvalenes.
The bibliography includes 150 references.

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I. INTRODUCTION

A new branch of synthetic organic chemistry and the chemistry of coordination compounds (associated with solid state physics), whose task is to synthesise and investigate new materials, which have been called organic metals, has developed vigorously during the last decade. Synthetic organic metals are highly anisotropic and in a certain temperature range behave like "true" metals; on the other hand, they have many unusual electrical, magnetic, and electronic properties[1-4].

The range of compounds on the basis of which synthetic metals can be obtained is fairly wide; further new substances, which are the principal components of organic metals, are being continually synthesised.

Many new studies (their number is increasing rapidly) of square planar transition metal complexes, which also exhibit the properties of one-dimensional synthetic metals under certain conditions have been published[5-8]. The dithiolate complexes of transition metals[9,10] and phthalocyanine[12,14] and porphyrin[11,13] derivatives are being widely investigated. Research into polymeric and electrically conducting materials is developing particularly vigorously. A realistic hope for the creation of fundamentally new technological materials has been a stimulating factor in this field[15-17]. A series of purely inorganic compounds also exhibit metallic conductivity [18,19].

The largest and vigorously developing class of compounds consists of organic metals based on radical-ion salts (RIS) and charge-transfer complexes (CTC) of various electron-donating and electron-accepting compounds. Among numerous thoroughly investigated radical-anion salts based on tetracyanoquinodimethane (TCQM) [20] and other electron acceptors[21], the organic metals which conduct electric current most effectively contain quinolinium, acridinium, and phenazinium cations and are radical-ion salts with a partially reduced TCQM molecule. The conduction in these salts takes place via a stack of TCQM radical-anion species.

Organic metals consisting of compounds with two conducting stacks (electron-donating and electron-accepting) have been thoroughly investigated. In this group of charge-transfer complexes, the salt TTF.TCQM (where TTF = tetrathiofulvalene) and all possible TTF derivatives capable of forming radical-ion salts with TCQM (and other organic acceptors) have been most thoroughly investigated[2,3,23]. CTC or RIS with TCQM have been obtained for the majority of electron-donating compounds listed in Table 1. Many important features characteristic of organic metals have been established precisely on the basis of the study of the radical-ion salts of certain TTF derivatives and other electron donors with TCQM. This has been reflected in a series of review publications[3,4,22,24,25] covering extensive factual data.

The latest advances in the field of organic metals are associated with the study of the radical-cation salts based on tetrathiofulvalenes, tetrathiotetracenes, and other heteroaromatic compounds in which conduction takes place solely via a stack of organic electron-donating molecules. These compounds proved to be the most convenient models for the investigation of the nature of organic metals and their transport properties[3,4,30].

Numerous radical-ion salts of TTT,[26] have been obtained in the series of tetrathiotetracenes TST,[27,28] and TTeT.[29]† The salts $(TST)_2Cl(Br)$ have record conductivities at room temperature ($\sigma = 2\times10^3\ \Omega^{-1}\ cm^{-1}$) and their metallic state is stable down to 1.5 K.[27] These results have been described in a number of reviews[3,30,31].

This review deals with organic metals comprising only tetrathiofulvalenes with inorganic anions. The first organic superconductors based on sulphur- and selenium-containing TTF derivatives have in fact been obtained among compounds of this series[32,33].

II. ORGANIC METALS BASED ON ELECTRON-DONATING COMPOUNDS. CONDITIONS GOVERNING THE EXISTENCE OF ORGANIC METALS

The principal trend in the development of the synthetic chemistry of organic metals is associated with the formation of new heteroaromatic compounds[34,35], with the introduction of various substituents into electron-donating and electron-accepting compounds and the study of the influence of these substituents on the conducting properties[36], and with the replacement of sulphur by selenium[37] and tellurium[38] in compounds of a single series. The endeavour to obtain a series of sulphur-, selenium-, and tellurium-containing compounds

† The abbreviations are defined in Table 1 (Ed. of Translation).

is due to the characteristic features of the structure of organic metals: the possibility of the movement of an electron through a stack of organic molecules is due to the overlap of the wave functions of the unpaired electrons of the heteroatoms and such overlap increases with increase in the size of the heteroatoms in the organic compound.

Table 1. Electron-donating compounds from which organic metals have been obtained.

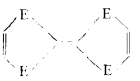
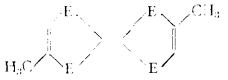
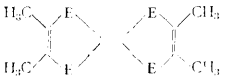
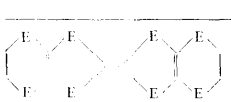
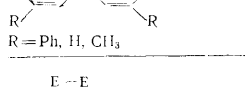
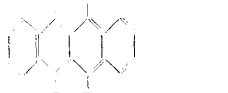
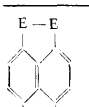
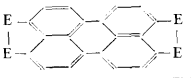
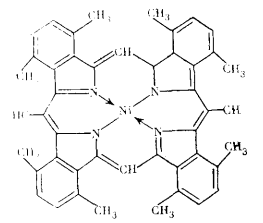
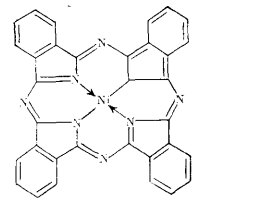
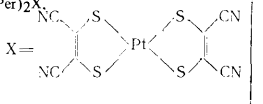
Formula	Name of compound	Refs.
	E = S, tetrathiofulvalene (TTF) E = Se, tetraselenofulvalene (TSF)	[42] [42]
	E = S, dimethyltetrathiofulvalene (DMTTF) E = Se, dimethyltetraselenofulvalene (DMTSF)	[42] [42]
	E = S, tetramethyltetrathiofulvalene (TMTTF) E = Se, tetramethyltetraselenofulvalene (TMTSF)	[42] [42, 43, 44, 150]
	E = S, tetrathiomethoxytetrathiofulvalene (TTMTTF) E = Se, tetraselenomethoxytetraselenofulvalene (TSMTSF)	[42] [42]
	E = S, hexamethylenetetrathiofulvalene (HMTTF) E = Se, hexamethylenetetraselenofulvalene (HMTSF) E = Te, hexamethylenetetratelluro-fulvalene (HMTTeF)	[42] [42] [45]
	E = S, dibenzotetrathiofulvalene (DBTTF)	[42]
E = S, Se: R = R′ = H, CH_3; R = H, R′ = CH_3 E = Te: R = R′ = H	E = Se, dibenzotetraselenofulvalene (DBTSF) E = Te, dibenzotetratellurofulvalene (DBTTeF)	[37, 46] [38]
	E = S, bis(ethylenedithiolo)tetrathio-fulvalene (BEDT-TTF) E = Se, bis(ethylenediselenoslo)tetra-selenofulvalene (BEDS-TSF)	[47] [48]
	Tetraformyltetrathiofulvalene (TFTTF)	[49]
R = OCH_3, H	E = S, dinaphthotetrathiofulvalene (DNTTF) E = Se, dinaphthotetraselenofulvalene (DNTSF)	[50] [50]
 R = Ph, H, CH_3	E = O, bipyranylidene (BP) E = S, bithiopyranylidene (BTP) E = Se, biselenopyranylidene (BSP) E = Te, bitelluropyranylidene (BTP)	[51] [51, 52] [53] [54]
	E = S, tetrathiotetracene (TTT) E = Se, tetraselenotetracene (TST) E = Te, tetratellurotetracene (TTTeT)	[55] [56] [29, 57]
	E = S, tetrathioanthracene (TTA) E = Se, tetraselenoanthracene (TSA)	[58] [58]

Table 1 (cont.)

Formula	Name of compound	Refs.
	E = S, tetrathionaphthalene (TTN)	[59]
	E = S, tetrathioperylene (TTP) E = Se, tetraselenoperylene (TSP)	[60, 61] [62]
	Octamethylenetetrabenzo-porphyrins (OMTBP)	[11, 13]
	Phthalocyanines (PC)	[12, 14]
Naphthalene (Naphth)	$(Naphth)_2PF_6$	[63]
Naphthalene Pyrene Fluoranthene	$(Arene)_2X$, X = PF_6^-, AsF_6^-, SbF_6^-, or BF_4^-	[15, 64]
Perylene (Per)	$(Per)_2(PF_6)_{1.1}.0.8CH_2Cl_2$ $(Per)_2(AsF_6)_{1.1}.0.7CH_2Cl_2$ $(Per)_2(PF_6)_{1.4}.0.6THF$ $(Per)_2(AsF_6)_{1.5}0.5THF$ $(Per)_2X$, 	[65] [65] [65] [65] [66]

Both electron-donating and electron-accepting compounds which are components of organic metals have a number of characteristic features[3,39,40], which have been established as a result of the investigation of extensive experimental data; the conditions governing the existence of the stabilised metallic state are constantly being extended and refined.

Table 1 presents the principal classes of heterocyclic electron-donating compounds from which organic metals have been obtained at the present time and are being investigated. The molecular and crystal structures of the components of organic metals must satisfy the following requirements.

(1) Their molecule must be planar in the neutral and ionic states; there is a possibility of a slight deviation (2-4°) from planarity of the ring, which creates conditions for the closest packing of the molecules in the crystal. The intermolecular interaction of the components in the conducting organic stack takes place via the overlap of the molecular π orbitals and is described by the overall wave functions of the unpaired electrons delocalised along the entire molecule.

(2) Their molecules must be symmetrical in order to eliminate the possibility of the appearance of a high random potential which might cause a transition of the system to the dielectric state. A weak electronic or structural disorder may stabilise the metallic state.

(3) The compounds considered must be packed in regular stacks. The movement of electrons takes place along the stack of organic molecules more readily than in the other two directions (the substances are anisotropic in the crystal state).

(4) The distances between the molecules in the stack must be identical and minimal to ensure the non-activated movement of electrons along the stacks.

(5) Apart from the shortened distances between the molecules within the stack, shortened distances between individual stacks are necessary for the stabilisation of the metallic state down to low temperatures and for the occurrence of the superconducting transition.

The electronic structures of the compounds must also have a series of characteristic features.

(1) The presence of unpaired electrons in the system is essential.

(2) Partial charge transfer must take place. Moderately strong electron donors and acceptors satisfy this criterion. The difference between the oxidation-reduction potentials of the electron donor and acceptor must be minimal[39,41].

(3) A minimal Coulombic repulsion energy is necessary to destabilise the transition to the Mott insulator state[39,41].

III. ORGANIC METALS AND SUPERCONDUCTORS BASED ON TETRATHIOFULVALENE DERIVATIVES

1. Organic Metals Based on Unsubstituted Tetrathiofulvalene and Tetraselenofulvalene With Inorganic Anions

The synthesis in 1970 [67] of tetrathiofulvalene, a heterocyclic compound, initiated the study of the enormous class of compounds based on it[2,3]. The crystals of neutral TTF are made up[68] of stacks of its molecules packed in such a way that the character of the structure predetermines the possibility of the insertion of small anions in the channels between the TTF stacks.

Interesting studies have been made on the radical-ion salts of unsubstituted TTF with the halogens. TTF derivatives with the singly charged Cl^-, Br^-, and I^- anions can be obtained by the direct oxidation of standardised TTF solutions in acetonitrile or CCl_4 with standard solutions of Cl_2, Br_2, and I_2 in the same solvents[69,70]. The photochemical reaction

$$TTF + CCl_4 \xrightarrow{h\nu} (TTF)Cl_n$$

can yield TTF chlorides[71]. TTF halides can also be obtained in the electrochemical generation of the TTF^+ radical-cation with subsequent addition of an alkylammonium salt containing Cl^-, Br^-, or I^-.[69] Under certain conditions, there is a possibility of the reverse reduction of the TTF^+ radical-cation with formation of the Br_3^- anion and the initial TTF [72]:

$$TTF^+ + Br^- \rightarrow TTF^0 + Br_3^-.$$

A characteristic feature of the reaction of TTF with the halogen is the formation of the compound $(TTF)X_n$, where $X = Cl^-$, Br^-, or I^- with different values of n. For $n = 1$, one electron is removed from each TTF molecule and the radical cation salt $(TTF^+)X^-$ with complete charge transfer is formed. When $n = 2$, dicationic salts are obtained, two electrons are removed from each TTF molecule on oxidation, and the salt $(TTF)^{2+}X_2$ is produced[69]. However, the number of electrons transferred from an electron-donating TTF molecule to the acceptor is frequently non-integral and is actually less than unity. For $n < 1$, compounds with different stoichiometric compositions are obtained and n can vary continuously within a certain range, while the physical properties of the compound do not change significantly.

The compounds $(TTF)X_n$ where X = halogen and $n < 1$, have been isolated and characterised in detail[69] and the parameters of their unit cell have been published. The phase with n in the range $0.7 < n < 0.8$, obtained for all three halogens indicated, is the most stable[69]. The structure of compounds having this composition [and in general of all the non-stoichiometric compounds $(TTF)X_n$] is characterised by the presence of two independent sublattices: the cationic sublattice consisting of TTF molecules packed regularly in stacks and the anionic sublattice consisting of inorganic anions. The channels between the TTF stacks are filled with the Cl^-, Br^-, or I^- anions distributed with different densities, which determine the non-stoichiometric composition of the compounds $(TTF)X_n$. Fig. 1 presents the structure of the compound $(TTF)Br_{0.76}$;[70] $n = 0.76$ corresponds to the maximum Br^- content on $(TTF)Br_{0.71-0.76}$. The structure contains two separate sublattices; the first consists of stacks of TTF molecules arranged along the conducting axis and the anions Br^- are arranged in the channels between the TTF molecules (second sublattice). The unit cell parameters are constant in the range $n = 0.71-0.76$. The distances between the TTF stacks are regular and equal to 3.57 Å.

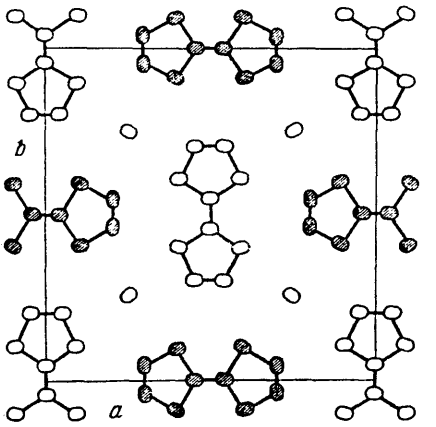


Figure 1. The structure of $(TTF)Br_{0.76}$.[70] Projection along the direction of the radical-cation TTF stacks.

The conductivities of the compounds $(TTF)X_n$ with halide ions are fairly high (Table 2). However, on decrease of temperature, all these compounds undergo the metal-, insulator transition at temperatures in the range 170–270 K and pass to the dielectric state. This is associated with a rearrangement of the structure of these compounds occurring as the temperature is reduced—the so-called Peierls transition takes place[78]. Despite the partial charge transfer, the conductivities of the compounds $(TTF)X_{0.67}$ with $X = ClO_4^-$ or BF_4^- are low, apparently because of the irregular packing of the electron-donating TTF molecules in the stack.

A series of non-stoichiometric TTF derivatives have been isolated electrochemically; one of them, namely $TTF(NO_3)_{0.55}$, has been characterised fairly completely and investigated[80].

Like the $(TTF)X_n$ with halide anions, this non-stoichiometric compound is made up of individual TTF stacks; the NO_3^- anions are distributed in the channels between the stacks of TTF molecules. While the compound has a fairly high conductivity at room temperature ($\sigma = 1200\ \Omega^{-1}\ cm^{-1}$), it undergoes a Peierls type metal → dielectric transition at 180 K.[80]

Apart from the non-stoichiometric compounds indicated in Table 2, radical-cation salts having the composition (TTF)X or $(TTF)_2X^{2-}$, where $X = Cl^-$, Br^-,[69] NO_3^-, BF_4^-, ClO_4^-,[82] $CuBr_3^-$, $AuCl_2^-$, $Cu(NO_2)_2^-$, $TiCl_4^{2-}$, $SnCl_6^{2-}$, or $RuCl_5^{2-}$,[84] the salts (TSF)X, where $X = Cl^-$[88] or I_3^-,[85] and the dicationic salts $(TTF)X_2$ or $(TTF)X^{2-}$, where $X = Cl^-$, Br^-,[69] NO_3^-, BF_4^-, ClO_4^-,[81,82] $CuCl_4^{2-}$, or $AuCl_4^{2-}$,[84] have been obtained.

The conductivities of the compounds (TTF)X with complete charge transfer are low and amount to 10^{-4}–$10^{-7}\ \Omega^{-1}\ cm^{-1}$. The compounds $(TTF)X_2$ are always insulators.

When TTF is oxidised by copper(II) chloride, several products are formed, depending on the solvent employed[81]; compounds with the copper-containing $CuCl_2^-$ anion are obtained (Table 2). Raman spectroscopic studies of these compounds have shown that the compounds $(TTF)_3(CuCl_2)_5$ contain both TTF^+ and TTF^{2+}; the latter is the only example of a compound with a mixed valence incorporating the TTF^{2+} dication. The compound $(TTF)(CuCl_2)$ contains only TTF^+, while $(TTF)(CuCl_4)^{2-}$ contains only the TTF^{2+} dication[81].

Table 2 Characteristics of the radical-ion salts based on unsubstituted tetrathiofulvalene and tetraselenofulvalene with inorganic anions.

Compound	σ, $\Omega^{-1}\ cm^{-1}$	T_t^*, K	Refs.
$(TTF)Cl_{0.77-0.91}$	4	271	[69, 71, 76]
$(TTF)Br_{0.71-0.76}$	300—550	180	[69, 73]
$(TTF)I_{0.69-0.72}$	100—450	200—270	[74]
$(TTF)(SCN)_{0.54}$	500—750	170	[75]
$(TTF)(SeCN)_{0.54}$	500—750	170	[75]
$(TTF)(NO_3)_{0.55}$	170; 1200	180	[80]
$(TTF)(BF_4)_{0.67}$	10^{-6}	—	[77, 82, 84]
$(TTF)(ClO_4)_{0.67}$	10^{-5}	—	[82]
$(TTF)_2(NO_3)$**	$5\cdot10^{-2}$	—	[81]
$(TTF)_3(CuCl_2)_5$	10^{-5}	—	[81]
$(TTF)CuCl_4$	10^{-5}	—	[81]
$(TTF)(CuBr_3)_{0.4}$	$4\cdot10^{-2}$	—	[84]
$(TTF)(CoCl_3)_{0.4}$	$4\cdot10^{-2}$	—	[84]
$(TTF)(PtCl_6)_{0.33}$	10^{-2}	—	[84]
$(TTF)_{0.6}[Ir(CO)_2Cl_2]$	10^{-2}	—	[79]
$(TSF)Br_{0.8}$	10	—	[88]
$(TSF)I_{0.8}$	300	—	[85]
$(TSF)(ClO_4)_{0.67}$	10^{-3}; 10^{-2}	—	[82, 110]
$(TSF)(BF_4)_{0.67}$	$5\cdot10^{-3}$	—	[82]
$(TSF)(NO_3)_{0.8\pm0.02}$	$5\cdot10^{-2}$	—	[82]

*T_t = metal–dielectric transition temperature.

**The composition of this compound apparently differs from $(TTF)_2(NO_3)$.

The oxidation of TTF in acetonitrile by the copper(II) salts CuX, where $X = ClO_4$, BF_4, or NO_3, leads to the formation of compounds having three different stoichiometric compositions depending on the reactant ratio: $(TTF)X_n$, (TTF)X, and $(TTF)X_2$[81,82] (Table 2).

Two types of packing of the TTF molecules have been observed[83] in the trichloromercurate radical-cation salts $(TTF)HgCl_3$, while the mercury-containing anions form either the dimers $(Hg_2Cl_6)^{2-}$ or polymer chains made up of $(HgCl_3)_n^{n-}$. The distance between the planes of the TTF molecules is 3.6 Å, which is analogous to the distances in $(TTF)Cl_{0.92}$[76] and $TTFBr_{0.76}$,[70] or 3.45 Å, as in the fully oxidised TTBr.[70] The structural analogies and X-ray diffraction data have led to the conclusion[83] that TTF is present in the $(TTF)HgCl_3$ salt in two different oxidation states. This has also been confirmed by Raman spectroscopy[83,84].

Very few compounds of the selenium analogue, namely the unsubstituted TSF, with inorganic anions have been investigated (Table 2), which is due to the difficulty of synthesising the initial TSF and the low conductivities of the compounds obtained. Thus, while the conductivity of the compound $(TSF)I_{0.8}$ at room temperature is comparatively high, if the temperature is reduced it behaves as a semiconductor[85] with an activation energy of conduction $E = 0.149$ eV.

In connection with the discovery of the superconductivity of the salts $(TMTSF)_2X$ ($X = BF_4$, ClO_4, NO_3 or PF_6),[105] the properties of the unsubstituted TSF combined with singly charged anions are of interest. The non-stoichiometric salts $(TSF)X_{0.67}$, where $X = ClO_4$ or BF_4, which are analogues of the salts of unsubstituted TTF,[77,84] have been obtained[82] by oxidising TSF with copper(II) salts. Salts having the 2:1 composition could not be isolated. X-Ray diffraction study of the salt $(TSF)(ClO_4)_{0.67}$[87] showed that the stack of the TSF molecules is divided into triads of molecules in terms of the type of overlap and that this apparently is the immediate cause of the significant decrease of the conductivity of this salt[86] (Table 2).

2. Organic Metals Based on Dibenzotetrathiofulvalene

The introduction of two benzene rings into the TTF molecule increases the extent of its π-electron system and the electron-donating capacity of dibenzotetrathiofulvalene (DBTT) then decreases compared with the unsubstituted TTF.[89] In the neutral state the DBTTF molecules are packed in regular stacks with interplanar distances between the molecules of 3.544 Å.[90]

The interaction of DBTTF with chlorine and bromine leads to the formation of mixtures of products with different stoichiometries[91,92], as for the unsubstituted TTF.[69] Individual single crystal compounds with chlorine were not isolated and compounds having the formula $(DBTTF)Cl_{0.7-1.0}$ were obtained. When DBTTF : Br = 1 : 1.2 in the reaction mixture, the compound $(DBTTF)Br_{1.2}$ is obtained; other compounds with bromine have the composition $(DBTTF)Br_{0.8-1.0}$.[91]

The reaction of DBTTF with iodine has been investigated in nitrobenzene and acetonitrile[91]. For the reactant ratio DBTTF : I = 1 : 0.5 in nitrobenzene, the compound $(DBTTF)_2I_3$ was isolated; further increase of the amount of iodine leads to the compound $(DBTTF)I_3$. In acetonitrile, the salt $(DBTTF)_2I_3$ was isolated for the ratio DBTTF : I = 1 : 2 and in the presence of a still greater excess of iodine (up to the ratio 1 : 10) the salt $(DBTTF)I_3$ was obtained. Compounds having the compositions $(DBTTF)I_{0.5}$ and $(DBTTF)I_{0.8}$ have been obtained in acetonitrile[94].

The compound $(DBTTF)I_3$ has been investigated by X-ray diffraction[93] (Fig. 2). Stacks made up of alternating groups of three DBTTF molecules and two linear I_3^- anions are characteristic of the structure. The linear I_3^- ions are accommodated in the channels between the mixed stacks. The S–S distance in the structure is shortened to 3.50 A; in addition, there are a series of shortened distances between S atoms and I_3^- groups. This structure of the compound $(DBTTF)I_3$ differs from that of the compounds of the unsubstituted TTF with the halogens, in the structure of which the stacks are made up solely of TTF molecules and the halogen atoms are distributed in the channels between them[76].

The conductivities of $(DBTTF)Cl_{0.7-1.0}$ and $(DBTTF)Br_{0.8-1.0}$ were measured using discs and amount to $10^{-2}-10^{-3}\ \Omega^{-1}\ cm^{-1}$. The conduction in the $(DBTFF)I_3$ single crystals investigated [95] is activated and the magnetic susceptibility of this compound varies in accordance with the properties of an infinite antiferromagnetic chain having an exchange integral $J = 100$ K. [95]

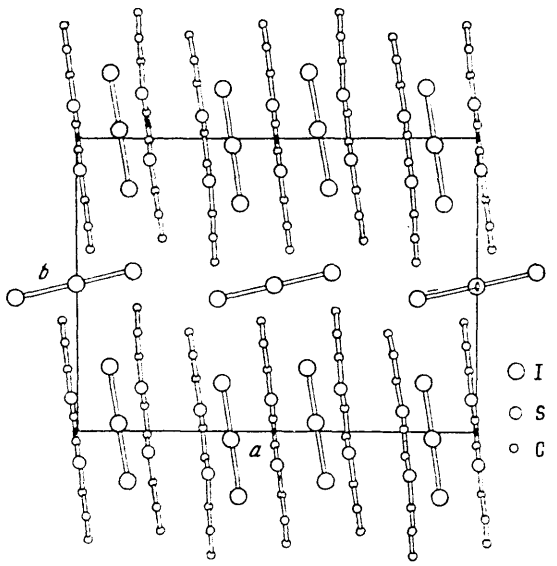


Figure 2. The structure of $(DBTTF)I_3$; [93] the side view of the DBTTF stacks with I_3^- anions accommodated in the channels between the stacks.

Metal halides and their complexes were used for the first time as oxidants for DBTTF. An interesting feature of these reactions is the fact that the oxidant behaves simultaneously as the complex forming anion or the anion can be formed in the course of the reaction[96,97]:

$$DBTTF + MX_4 \rightleftarrows DBTTF^+ + MX_3 + 2X^- \quad ;$$
$$MX_4 + 2X^- \rightleftarrows (MX_6)^{2-}$$
$$M = Sn,\ Te,\ X = Cl,\ Br$$
$$DBTTF + DBTTF^+ + (MX_6)^{2-} \xrightarrow{X=Cl} (DBTTF)_8\,(MCl_6)^{2-} \quad ;$$
$$\xrightarrow{X=Br} (DBTTF)_3\,(MBr_6)^{2-} \quad ;$$
$$M = Pt,\ Re,\ Sn,\ Te.$$

Table 3 presents the characteristics of the radical-ion salts obtained by oxidising DBTTF by various oxidants and the conductivities of the compounds obtained. The series of isostructural DBTTF compounds with doubly charged octahedral anions, having the general formula $(DBTTF)_8(MCl_6)_3^{2-}$, where M = Sn, Pt, Re, or Te, are of greatest interest. A characteristic feature of the structures of these compounds [97,98] is the presence of isolated cationic and anionic stacks arranged along the conducting axis of the crystal. Fig. 3 illustrates the lateral view of the cationic and anionic stacks in the $(DBTTF)_8(SnCl_6)_3$ structure. In the unit cell there are eight cations and three anions per period along the conducting axis of the crystal, the interplanar distance between the DBTTF molecules being identical throughout the stack and equal to 3.49 Å.

X-Ray diffraction study of the $(DBTTF)_8(MCl_6)_3$ complexes, where M = Sn, Pt, or Re, showed[98] that the presence of two sublattices—cationic with the single identical subperiod $c' = 3.49$ Å and anionic with the periods $c'' = 9.30$ Å for $SnCl_6^{2-}$,

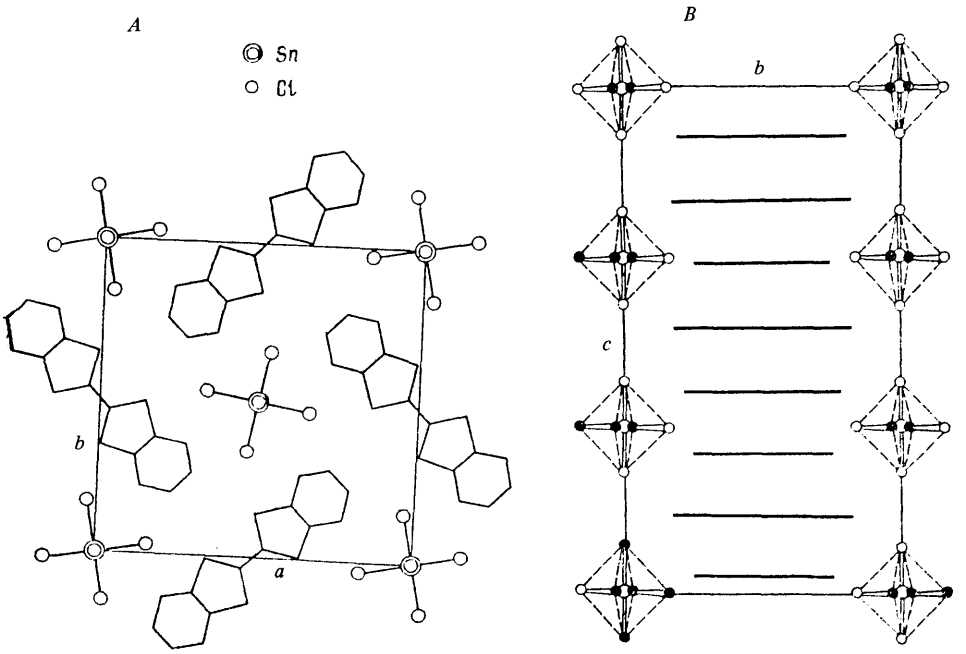


Figure 3. The structure of $(DBTTF)_8(SnCl_6)_3$; [98] *A*) view from above along the DBTTF stacks with the $SnCl_6^{2-}$ anion accommodated in the channels between the DBTTF molecules; *B*) side view of the cationic and anionic DBTTF and $SnCl_6^{2-}$ stacks.

9.52 Å for $PtCl_6^{2-}$, and 9.0 Å for $ReCl_6^{2-}$ —is manifested in the crystals of compounds of DBTTF with the MCl_6^{2-} anions. The ratios of the dimensions of the subperiods $c'':c'$ yield the ratios of the cationic and anionic components, which are 2.67:1, 2.73:1 and 2.59:1, and this also indicates the compositions of the complexes listed in Table 3. The small differences between the cationic components of these complexes, caused by the different dimensions of the octahedral anions which do not interact with one another, do not have a significant influence on the conductivities of the compounds. Conduction takes place via cationic stacks consisting of regularly arranged DBTTF molecules. In the compounds $(DBTTF)_8 \cdot (MCl_6)_3$ there are six radical-cation species and two neutral molecules for three doubly charged anions, so that the charge $(16-6):8=(10/8)e$ is formally localised on each molecule and the conductivity band is five-eighths filled[99].

Table 3. Characteristics of the radical-ion salts of dibenzotetrathiofulvalene with inorganic anions.

Salt	σ, Ω^{-1} cm^{-1}	T_t, K	Refs.
$(DBTTF)Cl_{0.7-1.0}$	10^{-2}—10^{-3}	—	[91, 92]
$(DBTTF)Br_{0.8-1.0}$	10^{-3}—10^{-4}	—	[91]
$(DBTTF)Br_{1.2}$	10^{-1}	—	[72, 91]
$(DBTTF)I_3$	10^{-3} *	—	[91, 93]
$(DBTTF)_2I_3$	10^{-2}	—	[91]
(DBTTF)2I	10^{-3}	—	[94]
$(DBTTF)(BF_4)_{0.8}$	10^{-2}	—	[103]
$(DBTTF)_{2.5}FeCl_4$	40 *	—	[102]
$(DBTTF)_{2.6}SnCl_6$	300—500 *	115	[97, 99]
$(DBTTF)_{2.73}PtCl_6$	300—500 *	115	[97]
$(DBTTF)_{2.53}ReCl_6$	0.5—1.0	—	[101]
$(DBTTF)_8(TeCl_6)_3$	0.5—1.0	—	[100]
$(DBTTF)_3SnBr_6$	40 *	—	[97]
$(DBTTF)_3PtBr_6$	40 *	—	[97]
$(DBTTF)_3ReBr_6$	10^{-2}	—	[101]
$(DBTTF)S(CH_3)_2PtBr_5$	10^{-3} *	—	[101]
(DBTTF)CuCl3	10^{-7}	—	[96]
$(DBTTF)_2PF_6(THF)_{0.3}$**	0.1 *	240	[104]
$(DBTSF)(TaF_6)_{0.61}$	20 *	140	[37]
$(DBTSF)(AsF_6)_{0.67}$	3 *	—	[37]
$(DBTSF)(SbF_6)_{0.72}$	0,5 *	—	[37]

* Measured for a single crystal.
** THF = tetrahydrofuran.

Measurements of the temperature variation of the conductivities of $(DBTFF)_8(SnCl_6)_3$ and $(DBTTF)_8(PtCl_6)_3$ single crystals showed that σ increases somewhat with decrease of the temperature T (by a factor of approximately 1.5); this is followed by a broad maximum, after which at 180 K the conductivity begins to fall in accordance with an activation law and the salt passes to the dielectric state at 113–117 K.[99]

Measurements of the temperature dependence of the magnetic susceptibilities of the compounds $(DBTTF)_8(MCl_6)_3$, where M = Sn, Pt, Re, or Te, demonstrated a metal-dielectric phase transition at 115 K.[99,100]

The replacement of MCl_6^{2-} by the larger MBr_6^{2-} anions leads to a series of isostructural compounds having the general formula $(DBTTF)_3MBr_6$ (M = Sn, Pt, or Re). It has been shown for $(DBTTF)_3SnBr_6$[98] that the cationic stack is divided into triads with different distances between the DBTTF molecules, amounting to 3.47, 3.44, and 3.44 Å. The conductivities of the $(DBTTF)_3MBr_6$ complexes are lower by an order of magnitude than those of $(DBTTF)_8(MCl_6)_3$; for discs, $\sigma = 10^{-2}\ \Omega^{-1}$ cm^{-1} for all the complexes, while for the single crystals of the compound $(DBTTF)SnBr_6$, we have $\sigma = 40\ \Omega^{-1}$ cm^{-1} at 300 K.

The replacement of one Br^- ion in $PtBr_6^{2-}$ by the dimethyl sulphide group leads to the formation of the singly-charged anion $Br_5PtS(CH_3)_2^-$ and of the charge-transfer radical-cation salt $(DBTTF)[Br_5PtS(CH_3)_2]$, the conductivity of the single crystals of which is $10^{-3}\ \Omega^{-1}$ cm^{-1}.[101]

The selenium analogue of dibenzotetrathiofulvalene, namely dibenzotetraselenofulvalene (DBTSF), has been obtained recently[37,46]. Its electrochemical oxidation in the presence of hexafluorophosphate anions leads[37] to the formation of the non-stoichiometric salts $(DBTSF)(TaF_6)_{0.61}$, $(DBTSF)\cdot(AsF_6)_{0.67}$, and $(DBTSF)(SbF_6)_{0.72}$ with single crystal conductivities of 0.5–20 Ω^{-1} cm^{-1} (Table 3). The properties of tetramethyldibenzotetraselenofulvalene (TMDBTSF), described by Johansen et al.[37], are of special interest in connection with the discovery of the superconductivity of TMTSF derivatives.

3. Organic Metals and Superconductors Based on Tetramethyltetraselenofulvalene

The greatest advance in the field of organic metals during the last three years has been the discovery of their superconductivity#.

The first organic superconductors were obtained in the form of 2:1 single crystal salts by the electrochemical oxidation of tetramethyltetraselenofulvalene in the presence of the corresponding tetra-alkylammonium salt[105,106,107]:

$$2TMTSF + (C_4H_9)_4X \xrightarrow[-e]{} (TMTSF)_2X.$$

The electrochemical method proved to be very suitable for the synthesis of single crystals of conducting compounds, because, during controlled oxidation or reduction by an electric current, the soluble donor or acceptor molecules are converted into less soluble oxidised or reduced complexes. The complexes of unsubstituted TTF,[80] TCQM[108], polycyclic aromatic compounds[54], and metal complexes of dithiolenes[109] have been obtained in this way. If electrochemical oxidation yields products with fairly high conductivities, they crystallise at the anode in the form of thin long needles or plates, since they can themselves function as the electrode, while the non-conducting compounds cover the anode in a thin film and electrocrystallisation stops.

The majority of organic metals are obtained nowadays by the electrochemical crystallisation method described by Mortensen and co-workers[105,110]. The purity of the initial electron-donating compounds, electrolytes, and solvents involved in the electrochemical process must meet very exacting requirements[105]. Special investigations of the influence of the donor purification conditions[110], the specific features of the solvents[111], and the construction of the electrochemical cell[112] on the quality of the crystalline salts formed have been carried out.

Chemical oxidation of TMTSF by copper(II) salts can yield (depending on the concentrations of the initial reactants and their ratio) salts having the compositions $(TMTSF)_2X$ or (TMTSF)X or the dicationic salts $(TMTSF)X_2$[82]:

$$TMTSF + CuX \rightarrow (TMTSF)_nX,$$
$$n = 2;\ 1;\ 0.5;\ X = BF_4,\ ClO_4,\ NO_3\ .$$

However, the resulting $(TMTSF)_2X$ crystals are then of a lower quality than in the electrochemical oxidation. Apart from the 2:1 salts, TMTSF salts of other compositions have

The properties of the superconducting salts $(DMTSF)_2X$ have been discussed in detail in "Proceedings of the International Conference on Low Dimensional Solids", Mol.Cryst. Liq.Cryst., 1982, **79**, Part II, 1–357.

been isolated[107]: $(TMTSF)Br_{0.8}$, $(TMTSF)(Br_3)_{0.8}$, $(TMTSF)_2(SiF_6)$, $(TMTSF)(TeF_5)$, and $(TMTSF)(R\text{-}SO_3)$, where R = *p*-tolyl or phenyl. The properties of compounds having other than 2:1 stoichiometry are those of semiconductors, while the salt $(TMTSF)_2(SiF_6)^{2-}$ is a dielectric[107].

Compounds having the composition $(TMTSF)_2X$, characterised by a wide range of variation of the physical properties from those of semiconductors to superconductors, are of greatest interest.

Table 4. Characteristics of the tetramethyltetraselenofulvalene salts $(TMTSF)_2X$.

Anion	σ^*, Ω^{-1} cm^{-1}	T_t, K	T_s, K	p_s, kbar	Refs.
ClO_4^-	400	***	1.4	****	[106, 107, 118]
ReO_4^-	400	180	1.3	9.5	[123]
BrO_4^-	300	200	***	***	[124, 130]
BF_4^-	540	40	**	12	[105, 107]
FSO_3^-	1600	86	3.5	6.5	[124—126]
NO_3^-	780	12	**	12	[105, 107]
$H_2F_3^-$	200	63	***	***	[127]
PF_6^-	540	12; 15	1.4	6.5; 8.5	[115, 117, 119, 121]
AsF_6^-	430	12; 15	1.4	9.5	[117, 132]
SbF_6^-	500	17	0.38	10.5	[117]
NbF_6^-	—	12	**	12	[117]
TaF_6^-	—	—	1.35	<11	[117]

Notation: T_t is the metal-dielectric transition temperature; T_s is the superconducting transition temperature; p_s is the pressure at which the compound undergoes the superconducting transition.

* At 300 K.
** There is no transition.
*** Not investigated.
**** At atmospheric pressure.

Table 4 presents the properties of the salts $(TMTSF)_2X$ with various singly-charged inorganic anions obtained hitherto. The anions present in these salts can be divided into the following groups in terms of their symmetry: octahedral (PF_6^-, AsF_6^-, NbF_6^-, SbF_6^-, TaF_6^-, TeF_6^-), tetrahedral symmetrical (BF_4^-, ClO_4^-, BrO_4^-, IO_4^-, ReO_4^-, and TcO_4^-), and tetrahedral asymmetric (FSO_3^- and $CF_3SO_3^-$); in addition there exist the triangular planar NO_3^- anion and the $H_2F_3^-$ anion. It is of interest to follow the differences between the compound $(TMTSF)_2X$ and other tetrathiofulvalene derivatives. All the compounds of the type $(TMTSF)_2X$ are isostructural. The almost planar TMTSF molecules are packed in stacks arranged exactly at right angles to the conducting axis of the crystal [146]. Fig. 4 [113] illustrates the structure of the compound $(TMTSF)_2ClO_4$, which is typical for the entire series of salts $(TMTSF)_2X$. Within the single stack, the molecules are arranged in a zigzag fashion with a shift equal to one quarter of the length of the molecule relative to one another (Fig. 4*a*, side view). Inside the stack, a weak dimerisation is observed: the distances between two neighbouring Se atoms of the TMTSF molecules in the stack are 4.021 and 3.96 Å; the distance between two other Se atoms are somewhat smaller (3.93 and 3.87 Å). A distinctive feature of these structures is the fact that the stacks are arranged in layers (Fig. 4*b*, view from above) with a very short Se-Se distance between the Se atom of neighbouring molecules in the layer, significantly smaller than the sum of the van der Waals radii of the Se atoms, which is 4.00 Å. [114] Such short Se-Se distances are responsible for the two-dimensional nature of this series of compounds (previously such shortened Se-Se distances between neighbouring stacks were found for the compounds TMTSF. .TCQM [115] and $(TST)_2Cl$). [31]

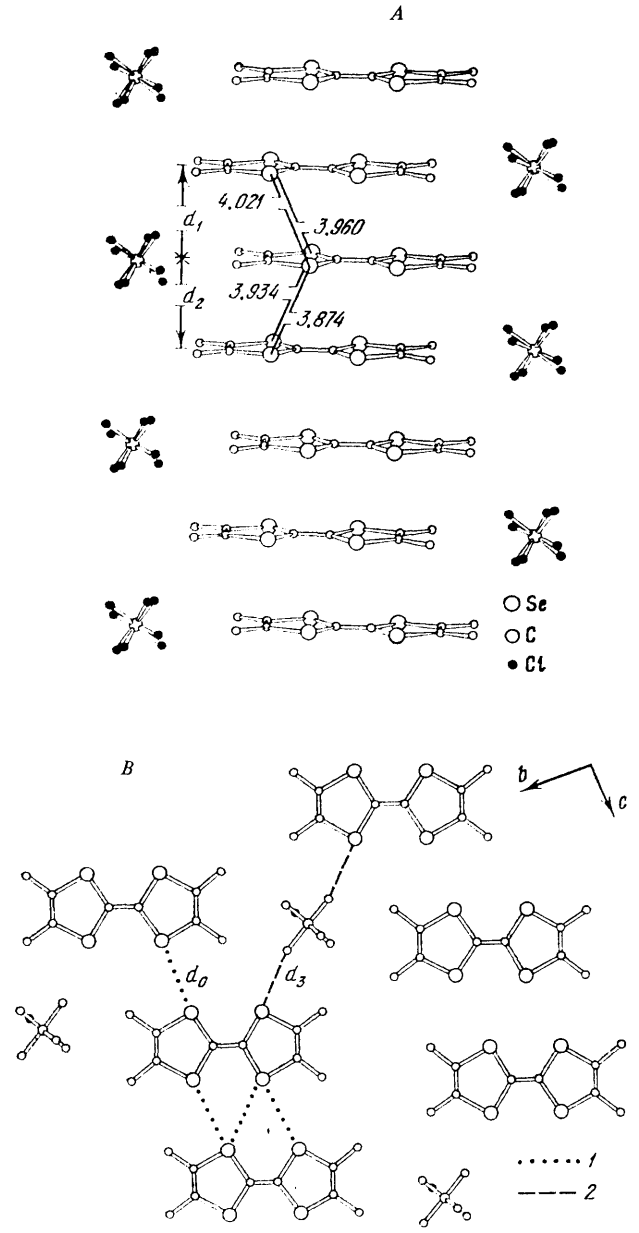


Figure 4. *A*) The structure of $(TMTSF)_2ClO_4$. [146] Side view of stacks of TMTSF molecules; the Se-Se distances between the TMTSF molecules within the stack are indicated; the ClO_4^- anions are located to one side; *B*) the structure of $(TMTSF)_2PF_6$; [113] the view from above the stacks of TMTSF molecules; the TMTSF molecules are evidently arranged in layers separated by PF_6^- anions; *1*) Se-Se distances in the layer of TMTSF molecules between individual stacks; *2*) Se-F distances.

Table 5. The distances between the stacks (d_0) of TMTSF molecules and within the stacks (d_1 and d_2) in $(TMTSF)_2X$ layers.

Anion	ClO_4^-		PF_6^-		AsF_6^-		ReO_4^-		FSO_3^-		$H_2F_3^-$		BrO_4^-		SbF_6^-	TaF_6^-
T, K	298 [146]	125 [116]	298 [113]	125 [116]	298 [132]	125 [116]	298 [123]	125 [123]	298 [125]	123 [125]	298 [127]	125 [127]	298 [124]	125 [124]	298 [117]	298 [117]
d_0, Å	3.77	3.655	3.88	3.741	3.90	3.789	3.827	3.70	3.866	3.829	3.816	3.735	3.875	—	—	—
d_1, Å	3.63	3.58	3.66	3.54	3.65	3.57	3.64	3.57	3.62	3.58	3.60	3.54	3.64	3.59	3.65	3.64
d_2, Å	3.62	3.57	3.63	3.59	3.62	3.57	—	—	3.63	3.57	3.60	3.53	—	—	—	—
d_3, Å	3.324	3.39	3.233	3.119	—	3.083	3.163	3.01	—	—	3.28	3.16	—	—	—	—
v_0, Å	694.3	673.7	714.3	681.3	719.9	698.3	710.5	—	695.3	677.7	671.2	650.0	707.2	689.8	737.0	735.6

Notation: d_3 is the minimum Se-O distance (in compounds with the ClO_4^- and BrO_4^- anions) or Se-F distance (for flourine-containing anions; v_0 is the volume of the unit cell; d_0 is the minimum Se-Se distance between TMTSF stacks in the layer; d_1 and d_2 are the interplanar spacings between TMTSF molecules within a single stack.

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

Table 5 lists the Se-Se distances in the stack and between the stacks for a series of salts $(TMTSF)_2X$. All these distances are significantly shorter than the sum of two van der Waals radii of the Se atom. For certain compounds (with PF_6^- and AsF_6^-), a weak dimerisation is observed within the TMTSF stacks ($d_2-d_1=0.03$ Å), but in the main the stacks are virtually not dimerised. With decrease of temperature, all the distances diminish, but the Se-Se distances between the stacks decrease much more than the Se-Se distances within the stacks (Table 5), i.e. the salts $(TMTSF)_2X$ become increasingly two-dimensional as the temperature is reduced[116].

Singly charged anions are arranged in the channels between the layers of TMTSF molecules; their arrangement is clearly seen from Fig. 4*b*. The centrosymmetric anions PF_6^-, AsF_6^-, SbF_6^-, TaF_6^-, and NbF_6^- can occupy only one position in the lattice[4,113,117]. The tetrahedral anions ClO_4^-, BF_4^-, ReO_4^-, BrO_4^-, SO_3F^-, etc., which lack central symmetry, can occupy two statistically non-equivalent positions in the lattice, which can vary with temperature. It has been suggested[117] that at low temperatures the ClO_4^- ions occupy only one position, but X-ray diffraction studies at 125 K [116] have shown that at least up to this temperature there is no ordering in the arrangement of the ClO_4^- ions. It has now been established that the differences between the structures of the anions and the changes occurring in their packing as the temperature is altered actually determine the entire wide variety of the properties of the salts $(TMTSF)_2X$.[4]

All the compounds of the $(TMTSF)_2X$ series have not unduly high electrical conductivities at room temperature, namely $\sigma \cong 400 \pm 100\ \Omega^{-1}\ cm^{-1}$ (Table 4), but, as the temperature is reduced, their conductivity increases very rapidly, reaching values of the order of $10^5\ \Omega^{-1}\ cm^{-1}$ for the majority of the salts before the transition temperature T_t.[107,119]

The salts of the octahedral anions (PF_6^-, AsF_6^-, SbF_6^-, TaF_6^-, and NbF_6^-) undergo the metal–dielectric transition at 12–17 K at normal pressures[107,117] (see Table 4). When an increased pressure is applied, the metal-dielectric transtion in compounds with the hexafluorophosphate anions is fully suppressed and all these compounds become superconducting at 0.9–1.3 K (Table 4).[117] It was shown for the first time in relation to the compound $(TMTSF)_2PF_6^-$ that the metal–dielectric transition is magnetic[120–122] and is associated with the antiferromagnetic ordering of the spins as the temperature is reduced with the formation of a spin density wave. The Peierls transition, which is usual for the organic metals investigated previously and is associated with a structural change in the conducting stack of organic molecules, is not observed for these compounds (the Peierls transition doubles the lattice period along the conducting axis of the crystal, which induces in its turn a periodic increase of the charge denisty along this axis, i.e. a charge density wave is generated[78]).

A different behaviour is characteristic of the salts $(TMTSF)_2X$ containing anions with a reduced symmetry (ClO_4^-, BF_4^-, ReO_4^-, NO_3^-, and FSO_3^-). At the usual pressure the salts $(TMTSF)_2ReO_4$,[123] $(TMTSF)_2FSO_3$,[124–126] and $(TMTSF)_2BF_4$,[105,107] undergo a sharp metal-dielectric phase transition at fairly high temperatures, namely at 180 K,[123] 86 K,[125] and 40 K[107] respectively (Table 4).

The metal-dielectric transition in the salt with the ReO_4^- anion has been attributed to the ordering of the arrangement of the ReO_4^- anions. At a pressure of 9.5 kbar the transition is suppressed and the compound undergoes the superconducting transition at 1.3 K.[123] It has been suggested that the metal–dielectric transition in systems with tetrahedral anions, similar to ReO_4^-, the behaviour of such systems under pressure and the influence of the position of the anion are associated with a special type of the Peierls mechanism which is based on the interaction of the conductivity electron with the ReO_4^- anion[123].

The salt $(TMTSF)_2FSO_3$ [125] differs from all other salts of this series by the fact that the FSO_3^- anion has a permanent dipole moment. The conductivity of the $(TMTSF)_2FSO_3$ single crystals[125] at 300 K is $\sigma = 1600\ \Omega^{-1}\ cm^{-1}$, which is higher than the usual conductivities of the series of $(TMTSF)_2X$ salts approximately by a factor of 4. With decrease of temperature to 86 K, a sharp metal–dielectric transition is observed and can also be noted in measurements of the magnetic susceptibility. It has been suggested[125] that the mechanism responsible for the metal-dielectric transition in this salt is associated with the generation of a charge density wave and not a

spin density wave. The physical properties of the salt are attributed to the influence of the permanent dipole moment of the FSO_3^- anion[125].

A qualtitatively different behaviour is characteristic of the compound $(TMTSF)_2NO_3$.[105,107] With decrease of temperature, the anions of this salt become ordered and the period of the unit cell is doubled along the conducting axis of the crystal.

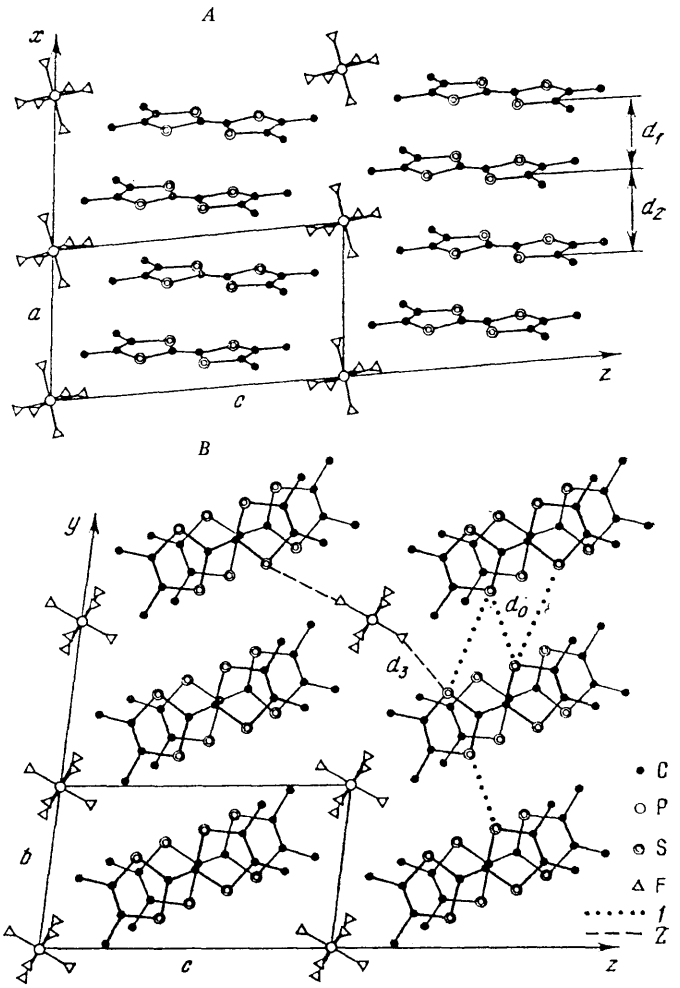


Figure 5. The structure of $(TMTTF)_2PF_6$: *A*) side view of the stacks of TMTTF molecules; the PF_6^- anions are distributed between the TMTTF stacks; *B*) view from above the layers of TMTTF molecules and PF_6^- anions; *1*) S–S distances between stacks of TMTTF molecules in the layer; *2*) S–F distances[135].

The order-disorder transition in the arrangement of the anions induces secondary effects in the electronic system of TMTSF. When pressure is applied, the metal-dielectric transition is suppressed, but the compound does not pass to the superconducting state. This is apparently associated with the fact that the NO_3^- anion is a relatively weak acceptor compared with the other anions investigated[107]. Yet another compound of the $(TMTSF)_2X$ series with the $H_2F_3^-$ anion has been obtained recently[127]. The $H_2F_3^-$ anion has a disordered arrangement and can occupy two possible positions around the centre of symmetry, each with a probability of 50%. This salt is isostructural with the other salts $(TMTSF)_2X$. Although the $(TMTSF)_2H_2F_3^-$ crystal has the smallest volume of the unit cell, the Se–Se distances in it are not the shortest (Table 5). The conductivity of this compound at room temperature is 200 Ω^{-1} cm^{-1}, but as the temperature is reduced, it undergoes the metal–dielectric transition (at 64 K).[127]

The salt $(TMTSF)_2ClO_4$ [105,107,118] is the only compound which does not undergo the metal–dielectric transition as the temperature is reduced and at 1.4 K at normal pressures it passes to the superconducting state. The principal difference between $(TMTSF)_2ClO_4$ and all other salts of this series is believed[106] to consist in the fact that the ClO_4^- ion has the smallest effective anionic radius. As a result of this, the interplanar spacings in the cationic stacks of $(TMTSF)_2ClO_4$ (Table 5) are smaller than in the other salts $(TMTSF)_2X$ under normal conditions and are close to the value which arises, for example, in $(TMTSF)_2PF_6$ under a pressure of 12 kbar.

The study of the resistivity[128] and elecronic heat capacity [129] of this salt as a function of the rate of cooling of the specimens showed a difference in its behaviour on rapid and slow cooling. The difference is associated with the fact that during rapid cooling the high-temperature disorder of the ClO_4^- anion persists and the length of the interchain linkage then diminshes[128,129].

The salts $(TMTSF)_2X$ with other anions, differing from those described in size (IO_4^- [110] and TcO_4^- [131]) and symmetry (TeF_5^- [107] and $CF_3SO_3^-$ [126]) are being investigated.

The main difference between $(TMTSF)_2X$ and all other compounds is the presence of layers of TMTSF molecules in them and shortened Se–Se distances between the stacks of individual TMTSF molecules, i.e. the presence of a definite degree of two-dimensional character. Since the interplanar spacings within the stack, d_1 and d_2 (Table 5), are ~3.6 Å (which is greater than the sum of two van der Waals radii of the carbon atom, equal to 3.4 Å),[114] one may conclude that electrical conduction takes place via short Se–Se contacts[132]. In the compounds $(TMTSF)_2X$, where $X = ClO_4^-$, PF_6^-, and AsF_6^-, the Se atoms are arranged in the stack at distances of 3.992, 4.005, and 3.992 Å respectively, while the corresponding distances between different stacks are 3.866, 3.924, and 3.988 Å (Table 5); thus the distances between the stacks are shorter by 0.05 Å (for AsF_6^-), 0.08 Å for (PF_6^-), and 0.126 Å (for ClO_4^-) than within the stack. It has been shown[116] that the structural changes occurring in the salts $(TMTSF)_2X$ on reduction of temperature are highly anistropic: the average distance between the stacks is shortened to a greater extent [116] (Table 5) (on average by a factor of between 1.6 and 2.1 for different anions) than the distances within the stack.

4. Organic Metals Based on Tetramethyltetrathiofulvalene

The observation of the metallic behaviour of the salts $(TMTSF)_2X$ down to low temperatures and of a transition to the superconducting state led investigators to turn to the S-analogues obtained previously[133,134], namely to salts of tetramethyltetrathiofulvalene (TMTTF) with various inorganic anions. Just as the elements S and Se show identical stoichiometries and structures, the structures of the salts $(TMTTF)_2Br$ and $(TMTTF)_2PF_6$ obtained previously[135] are identical with those of the salts $(TMTSF)_2X$; one could therefore expect that the study of the properties of the two series $(TMTSF)_2X$ and $(TMTTF)_2X$ with identical anions would help us to understand the causes of the similarities and differences

observed in the physical properties and to find real experimental parameters correlated with the superconductivity of the compounds. The study of sulphur derivatives has the advantage over the TMTSF salts that the synthesis of the initial compound TMTTF [42] is significantly simpler and does not involve the use of hydrogen selenide or carbon diselenide, which are difficult to obtain and are harmful. TMTTF salts are obtained either chemically[133,134] or electrochemically[136], similarly to the synthesis of TMTSF;[106] both procedures make it possible to obtain salts with the composition $(TMTTF)_2X$.

The oxidation of TMTTF by the halogens I_2, Br_2, and Cl_2 in solution in acetonitrile leads, like that of the unsubstituted TTF, to the formation of a large number of compounds of different compositions, whose conductivities vary within wide limits depending on the degree of charge transfer[133,134]:

Compound	σ, Ω^{-1} cm^{-1}	Compound	σ, Ω^{-1} cm^{-1}
$(TMTTF)_2I$	100	$(TMTTF)_2Br$	200
$(TMTTF)(I_3)_{0.45}$	50	$(TMTTF)Br_{0.8}$	100
$(TMTTF)I_3$	10^{-6}	$(TMTTF)(Br_3)_2$	—
		$(TMTTF)_2Cl$	10

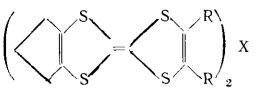
The individual TMTTF chlorides cannot be obtained by the direct oxidation of TMTTF with chlorine, but, using $SOCl_2$ as the oxidant, it is possible to isolate the chloride $(TMTTF)_2Cl$ [137] in the form of long thin needles (together with other reaction products).

By oxidising TMTTF with bivalent copper salts CuX_2 ($X = ClO_4$, BF_4, or NO_3), it is possible to obtain, as in the case of TTF and TMTSF,[82] three types of compounds depending on the reaction conditions (reactant ratio, concentration, and temperature): $(TMTTF)_2X$, (TMTTF)X, and $(TMTTF)X_2$.[82] The anion in CuX_2 must be capable of coordinating to Cu(I) less strongly than CH_3CN and be displaced by the latter from the coordination sphere of Cu(I).[81,82] Otherwise, TMTTF salts with a complex copper-containing anion are formed[138].

When TMTTF is oxidised by the inorganic salts $HgCl_2$,[139] $CuCl_2$,[138] and $MoCl_5$,[140] as for TTF and DBTTF,[96,97] an anion is formed, during the reaction in solution, whereupon crystals appear of both products with partial charge transfer of the type of $(TMTTF)_{1.25}Hg_2Cl_5^-$ with $\sigma = 10\ \Omega^{-1}$ cm^{-1} and $(TMTTF)_2CuCl_2$ with $\sigma = 1\ \Omega^{-1}$ cm^{-1} and compounds having the compositions $(TMTTF)HgCl_2$ and $(TMTTF)CuCl_3$ with $\sigma = 10^{-7}\ \Omega^{-1}$ cm^{-1}, in which complete charge transfer has taken place[138,139].

It is noteworthy that TMTTF complexes with partial charge transfer are, as it were, intermediates in the oxidation of TMTTF by inorganic salts and their isolation depends on the concentrations and ratio of the initial components. Thus, when TMTTF reacts with a 2.5-fold excess of $HgCl_2$ at the concentration $[TMTTF] = 2 \times 10^{-2}$ M, the radical-ion salt $(TMTTF)_{1.3}Hg_2Cl_5$ is formed; when the reactant ratio is smaller, the unreacted orange initial TMTTF is precipitated. Recrystallisation of $(TMTTF)_{1.3}Hg_2Cl_5$ from acetonitrile leads to further oxidation of TMTTF and the formation of the radical-ion salt $(TMTTF)(HgCl_3)$ and calomel. The interaction of TMTTF with $HgCl_2$ in dilute acetonitrile solutions at the concentration $[TMTTF] = 3 \times 10^{-1}$ M and the same reactant ratios does not lead to the product of the partial oxidation of TMTTF, the radical-cation salt $(TMTTF)HgCl_3$ being formed immediately and then crystallising in different modifications [139]. When TMTTF is oxidised by $CuCl_2$, the intermediate compound $(TMTTF)_2CuCl_2$ with partial charge transfer is formed and its formation is followed (possibly as a result of the catalytic oxidation of the $CuCl_2^-$ anion by atmospheric oxygen) by that of the anion $CuCl_3^-$ and of the corresponding radical-cation salt $(TMTTF)CuCl_3$, with complete charge transfer, in two modifications[138].

Preliminary studies of the salts of dimethyl-substituted TTF have shown that dimethyltetrathiofulvalene preferentially forms salts with inorganic anions having 2:1 or 1:1 compositions[110,147]. The conductivity of the latter is 50–300 Ω^{-1}cm^{-1} and there is a metal-dielectric transition at ~200 K. Asymmetric TTF derivatives also give rise to salts having the composition



where R = H or CH_3 and X are various fluorine-containing anions or ClO_4^-,[148,149].

From the standpoint of the study of physical properties, TMTTF salts having the composition $(TMTTF)_2X$ are of greatest interest, as for $(TMTSF)_2X$. The salts $(TMTTF)_2X$ are isostructural with the compound $(TMTSF)_2X$.[141] The degree of charge transfer in these salts, is determined, as for $(TMTSF)_2X$, by the valence state of the anion X^- and, for singly charged anions of the type BF_4^-, NO_3^-, PF_6^-, ClO_4^-, etc. the degree of charge transfer from each TMTTF and TMTSF molecule is 0.5; thus the conductivity band in $(TMTTF)_2X$ and $(TMTSF)_2X$ is three-quarters filled.

However, at normal pressures, the behaviour of the salts $(TMTTF)_2X$ differs from that of their selenium analogues[141]. Structurally the salts $(TMTTF)_2X$ are built up like the salts $(TMTSF)_2X$. The principal structural details can be seen in Fig.5, which represents the structure of the salt $(TMTTF)_2PF_6$.[135] Evidently here we have the same zigzag arrangement of the TMTTF molecules in the stack with a shift equivalent to one quarter of the length of the molecule along the conducting axis of the crystal (Fig.5*a*) and the stacks are arranged in individual layers (Fig.5*b*), while the PF_6^- anions are accommodated between layers of TMTTF molecules. However, the sulphur and selenium compounds differ significantly from one another in the distances between the individual molecular stacks in the layer.

In the salts $(TMTTF)_2X$ the interaction between neighbouring stacks in the layer can take place effectively via sulphur atoms in close proximity. Each TMTFF molecule has two sulphur atoms which are closest to the sulphur atoms of the next molecule. Table 6 presents the distances within the stack of TMTTF molecules (d_1 and d_2) and the S–S distances between neighbouring stacks. Evidently, these distances differ significantly for salts with different anions. The S–S distances within the stacks are not the same and differ slightly, i.e. the packing of the TMTTF molecules in the crystal is somewhat dimeric[136].

Table 6. Distances between TMTTF stacks (d_0) and within the TMTTF stacks (d_1 and d_2) for $(TMTTF)_2X$ salts[141].

Anion	Br^-	I^-	PF_6^-	ClO_4^-	BF_4^-	NO_3^-	SCN^-
d_0, Å	3.73	3.80	3.99	3.99	3.88	3.79	4.01
d_1, Å	3.53	3.54	3.62	3.59	3.56	3.56	3.56
d_2, Å	3.50	3.50	3.52	3.52	3.54	3.50	3.49
d_1-d_2, Å	0.03	0.04	0.10	0.07	0.02	0.06	0.07

All the interplanar spacings within the stack are less than the van der Waals radius of the sulphur atom, which is 3.6 Å. On the other hand, the S–S distances between the stacks are greater than 3.6 Å for all the salts $(TMTTF)_2X$ (Table 6).

Thus, these compounds are more one-dimensional than their selenium analogues. This is in fact responsible for the differences between the physical properties of the salts $(TMTSF)_2X$ and $(TMTTF)_2X$. The salt $(TMTTF)_2Br$, which has the smallest S–S distances and is least dimerised, is characterised by the highest conductivities among the series of compounds $(TMTTF)_2X$ (Table 7).

Table 7. Characteristics of the tetramethyltetrathiofulvalene salts $(TMTTF)_2X$ with different inorganic anions[136,141].

Anion	Cl^-	Br^-	I^-	PF_6^-	ClO_4^-	BF_4^-	NO_3^-	SCN^-
σ^*, Ω^{-1} cm^{-1}	10**	240	100	40	40	50	95	40
T_{max}, K	—	100	215	230	228	210	210	250
$\sigma_{max}/\sigma_{300}$	—	3.8	1.23	1.1	1.10	1.23	1.3	1.06
T_t, K	—	19	—	15	75; 10	41	160	—
T_t(K)/p(kbar)		24/25	10/30	30/30	—	—	—	—

Notation: T_{max} is the temperature at which the maximum conductivity of the specimen is observed; $\sigma_{max}/\sigma_{300}$ K is the ratio of the maximum conductivity to the conductivity at room temperature; T_t is the metal-dielectric transition temperature; T_t/p is the temperature of the phase transition in the specimen at a pressure p.

* At 300 K.

** According to the data of Zhilyaeva et al[137].

The salts $(TMTTF)_2X$ have significantly lower conductivities at room temperatures ($\sigma = 40$–300 Ω^{-1} cm^{-1}) (Table 7) compared with the conductivities of the salts $(TMTSF)_2X$. When the temperature is reduced, the conductivity of $(TMTTF)_2X$ initially increases slightly (Table 7) up to 210–250 K and then begins to fall. An appreciable increase of conductivity (by a factor of 3.8) is observed only for $(TMTTF)_2Br$ and its decrease begins at 100 K.

Different types of behaviour, depending on the structure of the anion, are characteristic of the salts $(TMTTF)_2X$, as for $(TMTSF)_2X$.

The salt with the non-centrosymmetric anion SCN^- undergoes a sharp metal-dielectric transition at 160 K.[141] Some change in conductivity of $(TMTTF)_2ClO_4$ is observed at 75 K; this transition is manifested clearly in measurements of the magnetic susceptibility and heat capacity. The conductivity curves for the salts $(TMTTF)_2BF_4$ and $(TMTTF)_2NO_3$ show no distinct transitions but, in the measurement of the magnetic susceptibility and heat capacity of $(TMTTF)_2BF_4$, a transition is clearly shown at 40 K.[141]

It has been shown[142] that the phase transitions observed for all the salts $(TMTTF)_2X$ with tetrahedral anions are not of the Peierls type and are more probably associated with the ordering of the anionic sublattice, which is manifested in the study of various physical properties of these salts.

Among the salts with centrosymmetric anions, only $(TMTTF)_2Br$ shows a clear phase transition at 19 K, while the transition of $(TMTTF)_2PF_6$, determined from magnetic susceptibility measurements, is at 15 K.

A correlation has been found[141] between the conductivities of the salts $(TMTTF)_2X$ and the S–S distances for salts with different anions: $Br^- > NO_3^- > I^- > BF_4^- > ClO_4^- > PF_6^- > SCN^-$ (Tables 6 and 7).

The physical properties of the salts $(TMTTF)_2X$ change abruptly when pressure is applied. The conductivities of the salts $(TMTTF)_2BF_6$ and $(TMTTF)_2ClO_4$ increase sharply up to 10^5 Ω^{-1} cm^{-1} at pressures up to 30 kbar and the metal–dielectric transition is observed at the very low temperatures of 10 and 30 K respectively (Table 7). The metallic state of $(TMTTF)_2Br$ under pressure is stabilised down to the very lowest temperatures and its conductivity reaches 10^6 Ω^{-1} cm^{-1} before the metal-dielectric transition. The influence of pressure on the properties of $(TMTTF)_2Br$ is extremely complex. At 22 kbar the metallic state is stabilised down to 10 K, after which there is a transition to the dielectric state. The same specimen under a pressure of 25 kbar does not undergo the transition to the dielectric state and may pass to the superconducting state[136,141,142]. However, all these effects change very markedly from specimen to specimen; when the temperature is reduced, some of their crystals at atmospheric pressure exhibit an increase of conductivity by a factor of 400. These characteristics of the behaviour of the salt $(TMTTF)_2Br$ have been studied in detail[142].

The behaviour of the salts $(TMTTF)_2X$ after the application of pressure can be explained by their significantly greater one-dimensional character[141,142] compared with $(TMTSF)_2X$; the salts $(TMTTF)_2X$ therefore exhibit only under pressure the properties characteristic of the salts $(TMTSF)_2X$ at atmospheric pressure.

5. Organic Metals Based on Bis(ethylenedithiolo)tetrathiofulvalene

A report has been published recently on the synthesis of a new class of organic superconductors based on bis(ethylenedithiolo)tetrathiofulvalene (BEDT-TTF).[33] It had been stated earlier[47] that the radical-ion salt BEDT-TTF.TCQM has a very high conductivity ($\sigma = 40$ Ω^{-1} cm^{-1}) for a pressed specimen. The first salt of this electron donor with an inorganic anion was obtained[143] by the electrochemical oxidation of BEDT-TTF in methylene chloride and has the composition $(BEDT\text{-}TTF)_2ClO_4.0.5CH_2Cl_2$. Its conductivity at room temperature is 25–30 Ω^{-1} cm^{-1}; as the temperature is reduced, σ increases, reaching 1000 Ω^{-1} cm^{-1} at 16 K, and then diminishes slightly but remains high at the helium temperatures: $\sigma = 650$ Ω^{-1} cm^{-1} at 1.4 K.[143] The anisotropy of the conductivity of the specimen is $\sigma_\parallel/\sigma_\perp = 0.9$ at room temperature, diminishing somewhat (down to 0.4) at 3 K. This enabled the authors[143] to claim that the compound is dimeric, which has been confirmed by structural studies[144]. The distance between the BEDT-TTF molecules within the stack is fairly large, but the S–S distances between neighbouring stacks are extremely short, amounting to 3.3–3.45 Å (compared with the van der Waals radius of the sulphur atom of 3.6 Å), which is responsible for the highly two-dimensional character of this compound. The superconducting transition has not so far been observed for this compound, but its conductivity remains metallic down to 1.4 K. This is the first observation of the metallic properties of an electron-donating sulphur-containing compound down to such a low temperature[143].

BEDT-TTF salts with various inorganic anions have been obtained by the electrochemical oxidation of BEDT-TTF in tetrahydrofuran (THF);[33] the BEDT-TTF salts with the ReO_4^- anion exhibit the most interesting properties. Compounds of several compositions, namely the thin acicular crystals of $(BEDT\text{-}TTF)(ReO_4)_2.THF$ and the lamellar crystals of the two salts $(BEDT\text{-}TTF)_4(ReO_4)_2$ and $(BEDT\text{-}TTF)_6(ReO_4)_4$, whose composition does not include the solvent, were obtained in the course of electrochemical oxidation. All the salts obtained

have different conductivity properties. Among these compounds, the salt $(BEDT\text{-}TTF)_4(ReO_4)_2$ is a superconductor with the superconducting transition at 2 K and a pressure of 4 kbar. It is of interest that the structure of this salt is very similar to that of $(TMTTF)_2X$ and $(TMTSF)_2X$. The BEDT-TTF molecules are also arranged in a stack in a zigzag fashion along the conducting axis and form layers made up of BEDT-TTF molecules between which the ReO_4^- anions are accommodated. The S–S distance along the stack is significantly longer than between individual stacks in the layer. However, there are differences: (1) the methylene groups CH_2 are displaced from the plane of the main molecules; (2) the ReO_4^- anions are ordered at room temperature, in contrast to the salts $(TMTSF)_2ReO_4$ or $(TMTTF)_2ReO_4$. The conductivity of $(BEDT\text{-}TTF)_4(ReO_4)_2$ at room temperature and at the usual pressure is 200 Ω^{-1} cm^{-1}, while on decrease of temperature the metal-dielectric transition takes place.

Thus yet another class of organic superconductors based on a sulphur-containing electron donor has been discovered[33]. According to preliminary data, the selenium analogue bis-(ethylenediseleno)tetraselenofulvalene (BEDT-TTSF), obtained by the same authors[145], give rise to 1:1 salts as a result of the electrochemical reaction in the presence of the ReO_4^- and ClO_4^- anions, the conductivities of single crystal specimens amounting to 10^{-1}–10^{-2} Ω^{-1} cm^{-1}. The authors noted the very low solubility of BEDS-TSF and the difficulties in electrocrystallisation associated with this factor.

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The data described show that the compounds based on tetrathiofulvalene derivatives examined here can give rise to salts with a wide range of properties—from a dielectric to a superconductor. However, the metallic state characteristic of these salts over a certain range of temperature is frequently unstable and the metal–dielectric transition takes place. The main task, namely the preparation of an organic semiconductor or an organic metal stable down to the very lowest temperatures, is therefore still far from being solved.

Theory shows that the metallic state cannot be stabilised in a one-dimensional system. Quasi-one-dimensional systems with a certain amount of two-dimensional or three-dimensional character are necessary. The metallic state in such systems can be unstable in relation to the superconducting transition and the compound can become a superconductor under appropriate conditions.

As shown above, the amount of three-dimensional character in quasi-one-dimensional organic metals can be increased by applying pressure. This can lead in its turn to partial or complete suppression of the low-temperature transition to the dielectric state.

However, the greatest possibilities in this respect arise in synthetic chemistry. The introduction of four (and even two) methyl groups into the TTF molecule makes it possible to obtain qualitatively new compounds having the composition $(TMTTF)_2X$, differing in their structure from the non-stoichiometric compounds $(TTF)X_n$, for which the 2:1 composition cannot be obtained.

Simple replacement of the S atom by the Se atom in the TMTTF molecule makes it possible to increase the degree of interaction between the stacks in the quasi-one-dimensional metal, i.e. to increase the amount of two-dimensional or three-dimensional character of the compound without altering the structure of the compound as a whole. This is apparently the cause of the appearance of superconductivity following the application of pressure to the salts $(TMTSF)_2X$, where $X = PF_6^-$, AsF_6^-, TaF_6^-, SbF_6^-, ReO_4^-, or FSO_3^-, while the compound $(TMTSF)_2ClO_4$ undergoes the superconducting transition at 1.4 K even at atmospheric pressure.

The increase of the number of sulphur atoms in the structure of the cation made possible in its turn the synthesis of the first superconductor based on a sulphur-containing donor: $(BEDT\text{-}TTF)_4(ReO_4)_2$.

By selecting the appropriate anion, it is possible to vary widely the physical properties in a single series of compounds. In conformity with the correlation found[131] between the unit cell parameters and the superconducting properties of the salts $(TMTSF)_2X$, it has been suggested that the salts of TMTSF with the POF_2^- anion or with the mixed anions ClO_4^-–BF_4^-, etc. may have properties closest to those of the superconducting salt $(TMTSF)_2ClO_4$.

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Characteristic Features of the Polymerisation of Acetylene and Its Derivatives

A.A.Matnishyan and V.M.Kobryanskii

The requirements which must be met by polymers with a conjugation system, used as organic semiconductors, are analysed. The characteristic features of ionic, radical and stereospecific polymerisation of acetylene and its derivatives are considered and the mechanisms of the destruction of the active centres in the ionic polymerisation as well as the methods of preparation of high-molecular-weight polymers are discussed.
The bibliography includes 52 references.

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I. INTRODUCTION

The polymerisation of acetylene and its derivatives is one of the fundamental methods for the synthesis of polymers with a conjugation system (PCS), which are beginning to be used at the present time as organic semiconductors and metals. Studies on the creation of organic semiconductors based on PCS can be referred to two periods. During the first period (from the beginning of the 1950s until the middle 1970s), hundreds of PCS of different structure were synthesised and extensive experimental data on their properties were accumulated. The polymers obtained had a whole series of interesting physicochemical and electrophysical characteristics. Some of them have found practical applications as thermostable materials and stabilisers in relation to the thermo-oxidative degradation of saturated polymers[1-7]. The work of A.A.Berlin has made an enormous contribution to the development of this field. During this period, the first semiconductor devices and photosensitive materials were created. However, the properties of the PCS did not satisfy the requirements of modern electronics, for which much more ordered polymers with a much higher molecular weight, forming films or crystals, are essential. The materials developed did not therefore find extensive practical applications.

The beginning of the second period of the synthesis of organic semiconductors and metals based on PCS is associated with the work of Wegner, Shirakava, and Heeger.

In 1968–1971 Wegner[8-10] demonstrated for the first time the possibility of creating polyconjugated single crystals based on substituted diacetylenes. The polymerisation was carried out in the solid phase with thermal, thermochemical, and radiation initiation. Later, whole series of single crystals of polydiacetylenes of different structure were synthesised. The study of the electrophysical and optical characteristics of the polymers obtained showed that they can be used as materials for non-linear optics. It was also shown that they are semiconductors with a high mobility of charge carriers. According to the estimates of different workers, the mobility of the carriers is in the range 10^3–10^5 $cm^2 V^{-1} s^{-1}$.

In 1971–1975 Shirakava and co-workers[11-13] were the first to synthesise a free highly ordered polyacetylene film on the surface of the $Al(C_2H_5)_3$–$Ti(OBu)_4$ catalytic system. The authors showed that a film in the *cis*-form is formed at −78 °C. Isomerisation to the more stable *trans*-form takes place either directly during the synthesis or during subsequent heat treatment. The films obtained have a metallic lustre and a conductivity between 10^{-9} Ω^{-1} cm^{-1} (for the *cis*-form) and 10^{-5} Ω^{-1} cm^{-1} (for the *trans*-form).

In 1977–78 Heeger and co-workers[14,15] established that the conductivity of polyacetylene films doped with powerful electron donors or acceptors increases by 12 orders of magnitude (from 10^{-9} Ω^{-1} to 10^3 Ω^{-1} cm^{-1}). The conductivity of an oriented polyacetylene film doped with AsF_5 was found to be 2×10^3 Ω^{-1} cm^{-1}.

These studies aroused enormous interest among physicists and chemists working in the field of organic semiconductors. They demonstrated the possibility, in principle, of creating organic metals and semiconductors whose properties are comparable to those of the corresponding inorganic materials. During this period, the number of studies on the synthesis and properties of PCS began to increase sharply. At the present time, many laboratories both in this country and abroad are engaged in research into this field. During recent years, a whole series of PCS which exhibit metallic conductivity on doping with powerful electron donors or acceptors have been synthesised. These are polyacetylene[11-15], polyphenylene[16-18], polypyrrole[19,20], poly(phenylene sulphide)[21,22], and polyheptadiyne[23]. This list is probably incomplete because the search for new polymers is still being continued. The study of the electrophysical characteristics of these polymers showed that, depending on the nature and concentrations of the doping agents, it is possible to obtain *n*- and *p*-type semiconductors or materials with metallic conductivity, which can find practical applications in new semiconductor devices, energy photoconverters, and organic accumulators and in the future also as substitutes for metals.

Analysis of the literature data shows that PCS must satisfy certain requirements in their practical utilisation as organic semiconductors and metals.

1. The polymers must have high molecular weights and must have a continuous conjugation chain.
2. The polymers must form films or crystals which are homogeneous and whose mechanical characteristics and purity satisfy the requirements of modern electronics.
3. In order to obtain specified electrophysical characteristics, it is essential to introduce into the polymers powerful electron donors and acceptors, which must be distributed uniformly throughout the bulk of the materials.
4. A high conductivity can be expected only for PCS in which the chemical structure and superstructure do not prevent intermolecular interactions.

5. The materials synthesised must retain their mechanical and electrophysical characteristics for a long time.

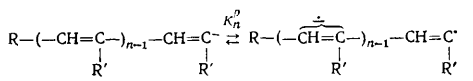
This review analyses the characteristic features of the polymerisation of acetylene and its derivatives and prsents certain experimental results in the synthesis of PCS.

II. POLYMERISATION METHODS

As already stated, studies on the polymerisation of monomers with a triple bond have been prosecuted since the end of the 1950s. In recent years a number of new original and review publications have appeared on the synthesis of PCS.[24–29] Analysis of the experimental results for the synthesis of high-molecular-weight polymers permits the conclusion that the classical methods of ionic and radical polymerisation do not lead to high-molecular-weight PCS; the latter can be obtained only in the presence of certain complex catalysts and variable-valence metal salts.

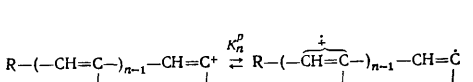
1. Ionic Polymerisation

We shall consider in greater detail the mechanism of the ionic polymerisation of acetylene derivatives. It follows from the literature data compiled in a review[24] that the anionic and cationic polymerisations of acetylene derivatives lead to the formation of polymers with a degree of polymerisation $n \cong 10$. In a study of the anionic polymerisation of phenylacetylene in the presence of butyl-lithium in hexamethylphosphoramide we showed[30,31] that the low molecular weight of the polyphenylacetylene formed is associated with electron transfer from the active centre to the conjugated chain:



This reaction results in the formation of a radical at the end of the chain and a radical-anion delocalised over the conjugation chain. Subsequently the radical is destroyed via a linear or quadratic mechanism, while the radical-anion is detected by ESR for a long time. The equilibrium constant of this reaction depends on the electron affinity of the radical formed and of the conjugated chain. The electron affinity of the radical is independent of the chain length, because the orbital in which it is located is orthogonal with respect to the orbitals of the conjugated chain. On the other hand, the electron affinity of the conjugated chain increases with chain length[32]. The probability of electron transfer (or the isomerisation of the active centres) should therefore increase with increasing degree of polymerisation.

Analogous features have been observed also in the cationic polymerisation of acetylene derivatives with the sole difference that the electron is transferred from a polyene chain to an active centre with formation of a radical at the end of the chain and a radical-cation delocalised over the conjugation system:



The equilibrium constant of this reaction depends on the difference between the ionisation potentials of the polyene chain and the radical formed. The ionisation potential of the radical is independent of chain length, while that of the conjugation system decreases with increasing chain length[32]. In the cationic polymerisation of acetylene derivatives the probability of electron transfer (the isomerisation of active centres) should therefore also increase with increasing degree of polymerisation.

The equilibrium constants of the electron transfer reactions in the anionic and cationic polymerisation of acetylene and phenylacetylene, calculated from data quoted in a handbook[32], are listed in Table 1. Evidently the anionic and cationic polymerisation of acetylene should be accompanied by the isomerisation of the active centres already in the first 2–3 units. In the polymerisation of phenylacetylene the isomerisation of the active centres should begin after the attainment of a degree of polymerisation $n \cong 5$–10. The increase of the degree of polymerisation on passing from acetylene to phenylacetylene is associated with the fact that the benzene ring stabilises the ion at the end of the chain.

The kinetics of the ionic polymerisation of acetylene derivatives have been analysed[33] taking into account the isomerisation reactions of the active centres and it was shown that the molecular weight distribution of the polymers formed is described by the equation

$$\rho(n) = f(n) \cdot \left(\prod_{i=1}^{n} \frac{1}{1+f(i)} \right), \qquad (1)$$

where $f(n) = (k_t/k_p M) K_n^p$, k_t is the rate constant for the linear termination of radicals, k_p the chain propagation rate constant, M the concentration of the monomer, and K_n^p the equilibrium constant of the electron transfer reaction.

Table 1. The equilibrium constants of the electron transfer reaction.

n	Anionic polymerisation		Cationic polymerisation	
	polyacetylene	polyphenylacetylene	polyacetylene	polyphenylacetylene
2	$7.95 \cdot 10^{-11}$	$7.85 \cdot 10^{-19}$	$2.35 \cdot 10^{2}$	$7.9 \cdot 10^{-13}$
3	$1.58 \cdot 10^{-9}$	$6.41 \cdot 10^{-12}$	$5.26 \cdot 10^{8}$	$3.3 \cdot 10^{-6}$
4	$1.7 \cdot 10^{12}$	$4.16 \cdot 10^{-8}$	$5 \cdot 10^{27}$	$4.55 \cdot 10^{-2}$
5	$4 \cdot 10^{17}$	$5 \cdot 10^{-5}$	—	$2.2 \cdot 10^{1}$
6	—	$9.5 \cdot 10^{-4}$	—	$1.05 \cdot 10^{3}$
7	—	$1.41 \cdot 10^{-2}$	—	$1.59 \cdot 10^{4}$
8	—	$9.7 \cdot 10^{-2}$	—	$1.1 \cdot 10^{5}$
9	—	0.312	—	—
10	—	2.16	—	—

Table 2 lists the number-average ($\bar{\Pi}_n$), weight-average ($\bar{\Pi}_w$), and z-average ($\bar{\Pi}_z$) degrees of polymerisation and the ratios $\bar{\Pi}_w/\bar{\Pi}_n$ and $\bar{\Pi}_z/\bar{\Pi}_w$ calculated by Eqn.(1) for the anionic polymerisation of phenylacetylene. Table 2 shows that, regardless of the ratio of the chain termination and propagation rate constants, low-molecular-weight polymers with a narrow weight distribution are formed. An increase of molecular weight can be achieved by decreasing the termination rate constant or by introducing into the acetylene molecule a substituent which stabilises the ion on the end of the chain.

From the ionic polymerisation scheme discussed above, it follows that the formation of high-molecular-weight polymers is possible only in the absence of the isomerisation reactions of the active centres. One of the possible polymerisation pathways without the isomerisation of the active centres may involve the formation of complexes with a conjugation

system directly in the course of chain propagation. We shall examine the mechanism of such a process in relation to the cationic polymerisation of acetylene derivatives. The reaction system should contain, apart from the monomer and initiator, the molecules of a powerful electron acceptor capable of forming stable donor–acceptor or radical-ion complexes with the polyene chain. In this case the propagation of the conjugation chain will be accompanied by the formation of complexes between the macromolecules and the acceptor molecules in which the electron density is displaced in the direction away from the polyene chain. Such macromolecules are incapable of giving up an electron to the active centre. In the prence of a sufficient number of electron acceptor molecules the cationic polymerisation should therefore proceed without the isomerisation of the active centres. Since strong Lewis acids behave simultaneously as electron acceptors and initiators of cationic polymerisation, when the process described above is carried out with their participation there is no need to employ an initiator and a separate complex-forming agent. The polymerisation is performed in the presence of large amounts of Lewis acids and the rate of initiation is regulated by introducing a specific amount of a cocatalyst. It is only necessary that the formation of complexes between the Lewis acids and the monomer should not prevent the chain propagation reaction.

Table 2. Parameters of the anionic polymerisation of phenylacetylene*.

	E_R = 1.6 eV					E_R = 1.3 eV				
k_t/k_pM	$\bar{n}_n$	$\bar{n}_w$	$\bar{n}_z$	$\frac{\bar{n}_w}{\bar{n}_n}$	$\frac{\bar{n}_z}{\bar{n}_w}$	$\bar{n}_n$	$\bar{n}_w$	$\bar{n}_z$	$\frac{\bar{n}_w}{\bar{n}_n}$	$\frac{\bar{n}_z}{\bar{n}_w}$
10^3	5.805	5.870	5.935	1.011	1.010	3.451	3.523	3.594	1.020	1.020
10^2	6.675	6.757	6.837	1.012	1.011	3.901	3.929	3.952	1.007	1.006
10	7.845	7.953	8.059	1.014	1.013	4.084	4.109	4.137	1.006	1.006
1	9.465	9.619	9.767	1.016	1.015	4.528	4.588	4.646	1.013	1.012
10^{-1}	11.83	12.06	12.29	1.020	1.019	5.065	5.111	5.157	1.009	1.009
10^{-2}	15.47	15.88	16.27	1.026	1.024	5.717	5.782	5.846	1.011	1.011
10^{-3}	21.58	22.38	23.12	1.037	1.033	6.562	6.642	6.720	1.012	1.011
10^{-4}	32.92	34.75	36.43	1.055	1.048	7.690	7.793	7.849	1.013	1.012
10^{-5}	56.79	61.69	66.16	1.086	1.072	9.252	9.399	9.541	1.015	1.015
10^{-6}	114.7	130.0	143.7	1.130	1.105	11.50	11.72	11.94	1.019	1.018

*E_R = electron affinity of the radical formed on electron transfer.

An analogous process can be carried out also in the anionic polymerisation of acetylene derivatives but in this case powerful electron donors must be used as substances functioning simultaneously as an initiator and a complex-forming agent. Such substances can be alkali metals.

Analysis of the model kinetics of ionic polymerisation with complex formation shows that the molecular weight distribution of the polymers formed is described by the equation

$$\rho(n) = f(n) \cdot \left[\prod_{i=1}^{n} \frac{(1 + K_{n-1}^{K})}{(1 + K_n^{K}) + f(i)} \right], \qquad (2)$$

where K_n^C is the complex formation equilibrium constant. It follows from Eqn.(2) that, when the equilibrium complex formation constant K_n^C is much greater than the equilibrium constant of the electron transfer reaction K_n^D, the polymerisation proceeds without the isomerisation of the active centres.

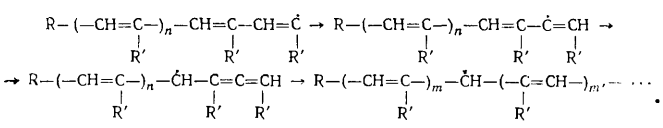
The possibility of obtaining polyacetylene films doped with AsF_5 directly in the course of the synthesis was first demonstrated in 1980.[34] The process was carried out by mixing gaseous acetylene and AsF_5 at different pressures and temperatures. Using an analogous procedure, we synthesised[35,36] SbF_5-doped films of polyacetylene and polyvinylacetylene with conductivities up to $10^{-2}\ \Omega^{-1}\ cm^{-1}$; the study of the polymerisation of vinylacetylene in the presence of various acceptors showed that the yield of the polymer decreases in the following sequence: $SbF_5 > H_2SO_4 > TiCl_4 > SnCl_4 >$ polyphosphoric acid[35,36].

The results show that the ionic polymerisation of acetylene derivatives in the presence of large amounts of a complex-forming agent is likely to be useful for the synthesis of organic semiconductors and metals because the complex formation process virtually constitutes doping of the polymer and makes it possible to obtain in a single stage highly conducting materials in the form of films. Such processes can be readily carried under technological conditions and make it possible to obtain films on various surfaces.

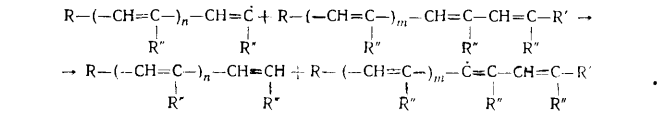
2. Radical Polymerisation

We believe that the radical polymerisation of acetylene derivates suffers from no fundamental limitations to the formation of high-molecular-weight polymers. However, it is known[6] that PCS are effective inhibitors of thermal and thermo-oxidative degradation, i.e. exhibit an enhanced affinity for radicals. In the radical polymerisation of acetylene derivatives there is therefore a possibility of the occurrence of side reactions the most important of which are as follows:-

(a) intramolecular isomerisation of the chain propagating radical:



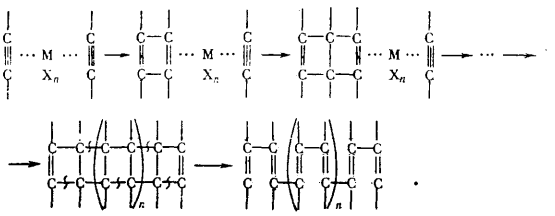
(b) intermolecular interaction of the chain propagating radical with the conjugated macromolecule via an addition or substitution mechanism:



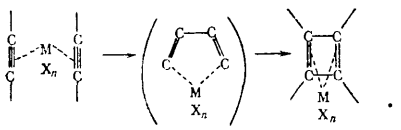
During these reactions, radicals delocalised over the conjugated system are formed and chain propagation ceases. The contribution of these reactions to the polymerisation process depends on the chemical structure of the monomer, the concentration, the temperature and the state of aggegation. The most suitable process for the formation of high-molecular-weight polymers is probably solid-phase polymerisation at low temperatures such as the polymerisation of single crystals of substituted diacetylenes. In solution, high-molecular-weight polymers are formed only when the polymerisation is accompanied by breaks in the conjugation in the system. For example, the polymerisation of vinylacetylene monomers[37,38] proceeds statistically at the double bond in the 1–4 positions. The breaks in the conjugation chain make it possible to obtain polymers with molecular weights of 10^4–10^6.[39,40] Subsequent heat treatment leads to rearrangements and the formation of a conjugated polymer.

3. Polymerisation of Acetylene and Its Derivatives in the Presence of Complex Catalysts and Variable-Valence Metals

There are few literature data on this problem, but the existing results suggest that, in the presence of these catalytic systems, the possibility of obtaining high-molecular-weight polymers is also associated with the absence of isomerisation reactions of the active centres. The polymerisation of phenylacetylene in the presence of metal carbonyls and various additives has been investigated[41-43]. The authors suggested that the chain propagation proceeds with formation of four-membered rings, which then isomerise to a polyconjugated polymer via the mechanism

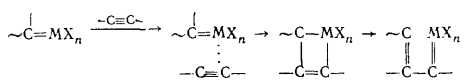


This mechanism is based on data concerning the formation of cyclobutadiene complexes in the presence of metal carbonyls. For example, it has been shown[47] that diphenylacetylene forms a cyclobutadiene complex in the presence of derivatives of iron tricarbonyl:



In the course of the reaction it is sometimes possible to detect intermediates. It is seen from the above scheme that the formation of high-molecular-weight polymers is associated with the formation of non-conjugated ladder macromolecules in the first stage.

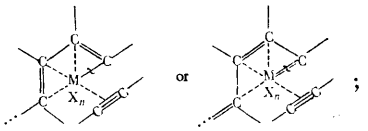
An intereresting polymerisation mechanism has been proposed in a large series of studies by Masuda and co-workers[28,29,45-47], who investigated the polymerisation of acetylene derivatives in the presence of various metal chlorides and carbonyls. They showed that the polymerisation of phenylacetylene in the presence of $W(CO)_6$ in CCl_4 under the influence of ultraviolet radiation makes it possible to obtain polymers with a molecular weight $\overline{M}_n \cong 80\,000$–$100\,000$, while 2-chlorophenylacetylene gives rise to polymers with $\overline{M}_w \cong 400\,000$ in the presence of $Mo(CO)_6$ under ultraviolet irradiation. The same workers showed that, by selecting the appropriate solvent, it is possible to obtain a polyphenylacetylene with $\overline{M}_n \cong 100\,000$ also in the presence of metal chlorides and their complexes. It has been suggested that the polymerisation proceeds via a stage involving the formation of a four-membered metal-containing cyclobutene unit:



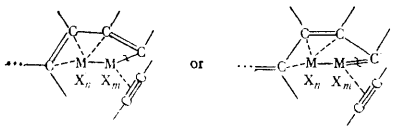
We believe that the formation of high-molecular-weight polymers in the polymerisation of acetylene derivatives in the presence of complex catalyst and variable-valence metals is associated with the tendency of the polyconjugated macromolecules formed to produce donor–acceptor complexes. It has already been stated than an increase in the conjugation chain length entails a decrease of the ionisation potential and an increase of the electron affinity of the macromolecules.

Therefore, regardless of the nature of the active centre and its linkage with the catalyst, the growing macromolecule also tends to form a coordinate bond with the catalyst. The strength of this bond should increase with increasing chain length.

In order to obtain high-molecular-weight polymers, it is necessary that the complex formed should not prevent the chain propagation reaction. Otherwise, cyclobutadiene and benzene derivatives or low-molecular-weight polymers are formed. The reaction complex can be illustrated schematically as follows:-



(3)



(4)

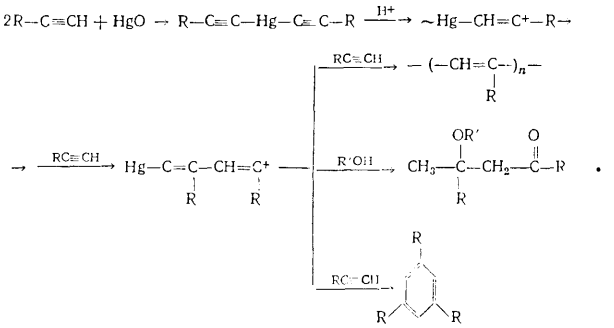
In such a complex the active centre is fixed on the catalyst via an additional coordinate bond with the conjugated system, which prevents its isomerisation and destruction. The available scattered literature data[48,49] concerning the structure of such complexes suggest that the preferential formation of high-molecular-weight polymers is observed when the catalytic centre contains several metal atoms [see Scheme (4)]. On the other hand, if the catalytic centre contains one metal atom, then low-molecular-weight products are formed [see Scheme (3)].

We investigated the polymerisation of acetylene, vinylacetylene, and their derivatives in the presence of palladium salts, mercury(II) oxide in conjunction with Lewis acids, and Ziegler and Latinger catalysts[50].

The catalytic system based on soluble palladium salts with ligands (pyridine and dimethylformamide) ensures a high yield of polymers in the polymerisation of propargyl derivatives, particularly with electron-accepting substituents[51,52]. The polymers obtained from bromo-substituted propargyl derivatives and their copolymers with diethylbenzene and divinylethynylmethanol have a conductivity of 10^{-8}–10^{-4} Ω^{-1} cm^{-1}. The covalently bound bromine atom in these polymers is apparently fairly labile and can be split off directly in the course of synthesis, forming complexes with the conjugation system.

The catalytic system consisting of a mixture of mercury(II) oxide and Lewis acids initiates a process which combines the features of ionic and coordination polymerisation. It proved to be effective in the polymerisation of acetylene and its derivatives. The polymerisation of acetylene in the presence of the homogeneous mercury(II) oxide–boron trifluoride etherate catalytic system has been studied for various component ratios. A soluble complex with an absorption maximum at 390 nm is formed in the first stage. At a concentration of the components of 10^{-4} M, the formation of a complex is observed immediately after the addition of the acetylene solution. The polymer is precipitated as a red-brown deposit which blackens on standing and contains residues of the catalyst. In the polymerisation of gaseous acetylene in the presence of a layer of catalysts deposited on a support, it was possible to grow films several millimetres thick. The polymerisation of vinylacetylene in the presence of the same catalytic system begins at a temperature as low as −70 °C. The yield of the polymer increases with increase of temperature.

Despite their inertness, propargyl derivatives polymerise almost quantitatively and the first stage involves the formation of mercury bisacetylides, which subsequently catalyse the polymerisation[50]. The polymerisation of phenylacetylene also proceeds via a stage in which mercury bisacetylide is formed. The mercury bisacetylide isolated is soluble in the monomer and has a high catalytic activity. It has been suggested that the polymerisation proceeds via a cationic mechanism. The formation of a σ-complex of mercury with the acetylenic bond loosens the latter and facilitates attack by the proton. In a simplified form the process can be represented by the following scheme:



In the presence of alcohol, it was possible to isolated the dimeric cation termination product, namely 3-methoxy-1,3-diphenyl-1-butanone, which confirms the validity of the above scheme.

It has been shown[27] that the $Co(NO_3)_2$–$NaBH_4$ catalytic system makes it possible to obtain a highly ordered polyacetylene, the degree of crystallinity of which is higher than that of the substance obtained by the Shirakava method. Polyacetylene films of any size on various surfaces can be obtained in the presence of this system†.

III. CONCLUSION

The data examined in this review show that a qualitative leap forward has been achieved in recent years as regards the creation of organic semiconductors and metals based on polymers with a conjugated system. Methods have been developed for the preparation of polymers in the form of films whose conductivity increases by 10–16 orders of magnitude after the interaction of powerful electron donors or acceptors. The electrophysical characteristics of polyacetylene, polyphenylene, and certain other polymers already make it possible to devise on their basis accumulators, photoconverters, and semiconductor devices.

Analysis of the mechanisms of the ionic, radical, and stereospecific polymerisation of acetylene derivatives has shown that the destruction of the active centres is associated with a decrease of the ionisation potential and an increase of the electron affinity of the polymer chain. Ionic polymerisation in the presence of a complex-forming agent and polymerisation in the presence of metal complex catalysts are most promising for the preparation of organic semiconductors and metals. The results presented suggest that procedures for the preparation of organic semiconductors whose parameters will enable them to compete with the corresponding inorganic materials will be developed in the next few years.

† See V.M.Kobryanskii and A.A.Matnishyan, "Materialy III Vsesoyuznogo Nauchnogo Seminara 'Ionika Tverdogo Tela'" (Proceedings of the IIIrd All-Union Scientific Seminar 'The Ionics of the Solid State'), Vilna, 1983, p.5.

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Transport Processes in Electrically Conducting Dispersely Filled Polymeric Composites

V.G.Shevchenko and A.T.Ponomarenko

The mechanisms of electrical conduction in polymeric composites with electrically conducting fillers are examined on the basis of effective medium, fluctuation tunnelling, and percolation models. The properties of the conducting fillers—metals, graphite, and technical carbon—are analysed. Factors influencing the electrical conductivity of the composites, in particular the methods of preparation of the filler and of the material, are discussed. The prospects for the utilisation of composites of this type are indicated.
The bibliography includes 62 references.

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I. INTRODUCTION

In connection with the increasing demands imposed by the technology and economic factors, many branches of industry have been faced in recent years with the increasingly acute problem of the manufacture of materials with a set of new properties. This applies particularly to materials which should combine the properties characteristic of semiconductors and metals and also polymeric materials. In principle, these requirements can be satisfied in two ways—either by synthesising polymers with a new chemical structure, for example, polymers with a conjugation system, and doping them or by introducing an electrically conducting filler (powders, metals, graphite, carbon black, etc.) into polymeric dielectrics. Both these procedures are well known from the literature. The creation of materials of this type naturally requires the knowledge of the structure and mechanism of the generation and transport of [current] carriers in the materials. Because of their chemical structure, an extensive literature has been devoted to polymeric materials with semiconducting properties[1,2], while electrically conducting polymeric composites have been studied to a much lesser extent at the present stage of development[3-6]. This review deals mainly with transport processes in electrically conducting polymeric composites.

The range of applications of such materials is fairly broad and the study of the existing and the creation of new electrically conducting materials therefore constitutes an extremely urgent task[7].

II. ELECTRICALLY CONDUCTING FILLERS

Various metals, graphite, and technical carbon (carbon black) can be used as electrically conducting fillers. Fig.1 presents typical relations between the resistivities ρ_v of the compositions and the concentration of the electrically conducting filler. At low concentrations ρ_v is close to the resistivity of the polymer, its value decreasing sharply subsequently and approaching ρ_v for the filler at higher concentrations. Fig.1 shows that organic fillers are usually more effective as electrically conducting additives than metallic powders. We shall consider the properties of various types of fillers.

1. Metallic Fillers

When metals (Cu, Al, Ni, Zn, Au, Ag) are introduced into a polymer, a fairly high conductivity is reached only at their high concentrations[3], because the surfaces of the particles of many of the available metals are in most cases coated by an oxide film, which hinders the transport of carriers between the filler particles. Furthermore, the density of the metal greatly exceeds that of the polymer, which results in a considerable increase of the weight of the composite. All these factors resulted in the use of metals only in certain instances: in compositions with various ceramics (the so-called cermets) in order to obtain high-resistance resistors[8] and also in electrically conducting adhesives used in the electronic industry in order to avoid the welding of components. In the latter case expensive colloidal silver must be used at fairly high concentrations (up to 70 wt.%) in order to obtain the required conductivities and this naturally limits the applications of such adhesives[9].

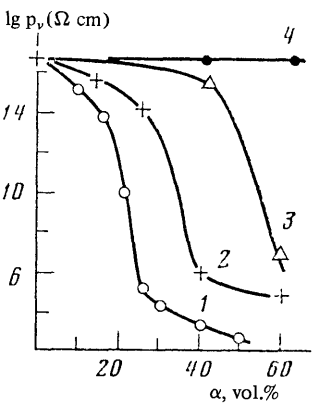


Figure 1. Dependence of the specific bulk-phase resistivity ρ_v of the composition based on low-density polyethylene on the concentration of electrically conducting fillers[3]: *1*) acetylenic carbon black; *2*) ZKA graphite; *3*) PAK-3 aluminium powder; *4*) zinc dust.

The use of special mixing procedures or the application of metallic particles of an unusual shape (in the form of scale, metallic leaf, dendrites, etc.) makes it possible to reduce their concentration necessary for the attainment of specific levels of conductivity[10,11].

The theoretical principles of the preparation of colloidal metals and composites based on them were developed approximately ten years ago[12,13]. Polymeric composites with highly dispersed metallic fillers have been obtained by electrolytic[13] and thermal[13,14] methods.

2. Graphite

It is known[15,16] that the crystal lattice of graphite consists of a set of planes in each of which the carbon atoms form a network of regular hexagons with a side of 0.418 Å.[17] The distance between the planes of the conjugated π-bonds is much greater (3.35 Å) and the planes are therefore weakly bound to one another and graphite can be readily cleaved. The conductivity of graphite in the plane of the layers σ_a is metallic and reaches $10^4\ \Omega^{-1}\ cm^{-1}$ at a concentration of carriers $n \cong 10^{19}\ cm^{-3}$ and their mobility $\mu \cong 10^4\ cm^2\ V^{-1}\ s^{-1}$.[16] The conductivity at right angles to the layers σ_c depends greatly on the perfection of the structure of the single crystal, the presence of impurities, and many other factors. For this reason graphites are classified as semimetals. The anisotropy of the electrical conductivity (σ_a/σ_c) varies within fairly wide limits: from 250 to 10^4. The natural graphite used as the conducting filler has a polycrystalline structure with a high content of amorphous carbon and the conductivity of such graphites is therefore low. Furthermore, the graphite particles are unable to form chain structures and the increase of the conductivity of the composites is therefore achieved by introducing high concentrations of the filler, which impairs the physicomechanical properties of the material[3]. For these reasons, natural graphite was not considered previously as a promising electrically conducting filler. However, data obtained recently concerning new methods of filling[18–20] may modify this view.

It has been observed recently that the introduction into graphite of powerful electron acceptors (SbF_5 and AsF_5), which form the so-called intercalated or layer graphite compounds, increases the conductivity of graphite to values exceeding that of the best conductor—copper. The employment of such compounds as conducting fillers appears to be extremely interesting in some cases[21].

3. Technical Carbon (Carbon Black)

The most widely used electrically conducting filler is carbon black (technical carbon). At the present time more than 90% of technical carbon manufactured and consumed consists of pitch carbon black but special varieties of acetylenic carbon black are most frequently employed as fillers[22]. X-Ray diffraction studies of the carbon black particles have shown that they consist of individual small crystalline cells of the graphite type. The disposition of carbon atoms in the layer is the same as in graphite crystals but the distance between layers is greater. The sites where the end faces of the parallel layers emerge on the surfaces of the particles have an increased energy and hence an increased adsorption capacity. This is in fact the reason for the ability of carbon black particles to form chains and network structures—the property referred to as "degree of structure" of the carbon black[5]. The active sections on its surface can also adsorb extraneous components (for example, oxygen) and the presence of the latter impairs the "degree of structure" of the carbon black. For this reason, the conductivity of the carbon black usually increases with decrease of the concentration of volatile substances[23]. Another factor which determines the conductivity of the carbon black is the specific surface which depends on the size and porosity of the particles.

Thus technical carbon (carbon black) which is effective as an electrically conducting filler must have the following characteristics: a large specific adsorption surface, a high porosity, a small particle size, a low content of volatile admixtures, and a high degree of structure[24]. It will be shown below that the conductivity of the composite is determined not only by the characteristics of the filler but also by the method of mixing of the components.

III. THE MECHANISMS OF ELECTRICAL CONDUCTION IN POLYMERIC COMPOSITES

Electrically conducting composites lack long-range order in the distribution of filler particles and such materials are therefore classified as typical disordered systems. The results obtained for disordered semiconductors and other systems can be used in the study of transport phenomena in the composites under consideration[25].

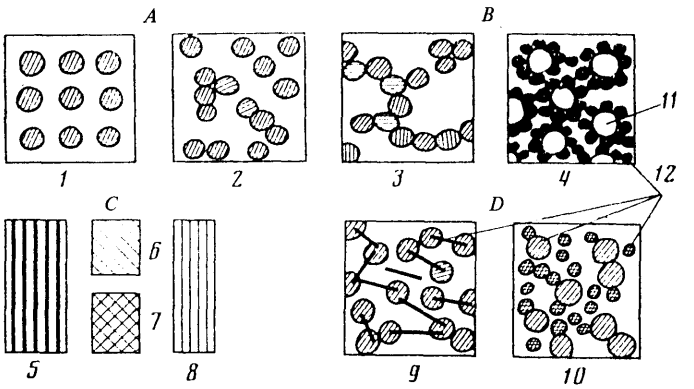


Figure 2. Different types of distribution of fillers in a polymer matrix: *A*) disperse systems [*1*) matrix mixture; *2*) statistical mixture]; *B*) structured disperse systems [*3*) two-component system; *4*) three-component system]; *C*) filler in the form of fibres, fabrics, and strips [*5*) layer structure; *7*) biaxially oriented structure; *6*) and *8*) monoaxially oriented structure]; *D*) mixed filler [*9*) fibre–sphere; *10*) two spheres]; *11*) dielectric; *12*) various forms of conducting fillers.

To a first approximation, it is possible to distinguish matrix systems, statistical mixtures, and structured compositions in terms of the nature of the distribution of the components[4]. In matrix systems one phase is continuous and at any concentration. In statistical mixtures the components are distributed at random and do not form regular structures. Systems whose components form chain, planar, or bulk-phase structures are classified as structured composites. Fig. 2 presents typical structures of composites and the distribution of the filler in the matrix.

In a number of studies theoretical calculations have been made to establish a relation between the properties of the components, on the one hand, and those of the composite, on the other. The early investigations of transport phenomena date back to 1892 when Rayleigh examined the conductivity of a matrix with a cubic packing of conducting spheres[26]. In the same year Maxwell proposed a mathematical analysis of systems containing spheres distributed at random in a continuous matrix[27]. Odelevskii proposed in 1951 a method for the calculation of the generalised conductivity of heterogeneous composites[28]. His relations can be used to calculate the electrical and thermal conductivities, magnetic permeabilities, and dielectric constants of composites. Such generalisation is possible because the equations describing the scalar and vector fields of these quantities are formally identical. The electrical conductivity of a matrix system (polymer matrix) is described by the equation

$$\sigma = \sigma_p\left(1+\frac{\alpha_f}{\frac{1+\alpha_f}{3}+\frac{\sigma_p}{\sigma_f+\sigma_p}}\right)$$

For a statistical mixture, we have

$$\sigma = \frac{(3\alpha_p-1)\sigma_p+(3\alpha_f-1)\sigma_f}{4}+\left[\frac{[(3\alpha_p-1)\sigma_p+(3\alpha_f-1)\sigma_f]^2}{16}+\frac{\sigma_f\sigma_p}{2}\right]^{1/2},$$

where α_p, α_f, σ_p, and σ_f are the concentrations and conductivities of the polymer and filler respectively.

The Lorentz–Lorenz and Lichtenecker formulae are also available for the calculation of the conductivities of mixtures[4,8,29,30].

It is noteworthy that none of the expressions enumerated above employ any specific mechanism of the transport of carriers in the composites but are based on the "effective medium" model. Reliable results are therefore obtained with the aid of the above computational formulae only in cases where σ_p and σ_f do not differ by a factor greater than 10^2. In many composites with a polymer matrix, this condition is not observed: the conductivity of polymers [polyethylene, polystyrene, and poly(vinyl chloride)] is 10^{-12}–10^{-16} Ω^{-1} cm^{-1},[4] while that of carbon black is 10 Ω^{-1} cm^{-1} [22] and that of graphite is up to 10^4 Ω^{-1} cm^{-1}.[16] Thus new approaches are necessary for the description of the properties of electrically conducting polymeric composites.

There is so far no unanimous view concerning the mechanism of electrical conduction in filled polymers. The following views are the most common: (a) charge transfer is based on the direct contact between the particles of the electrically conducting filler distributed in the specimen in the form of chains[31,32]; (b) charge transfer takes place not only on direct contact between the conducting particles, but also as a result of electron tunnelling through the dielectric layers of the polymer[33]. The level of the experimental technique does not so far permit an unambiguous answer to the question whether the sharp increase of conductivity with increase of the concentration of the filler is associated with the direct contact of the filler particles with one another or whether a mutual approach of the conducting particles to within distances necessary for the achievement of the tunnel effect is sufficient.

In order to estimate the dominant type of contact, analysis of the dependence of the current on the potential is frequently employed[4]. To a first approximation, this dependence is described by an equation of the type

$$i = cu^n,$$

where c and n are constants. The direct proportionality between the current and the potential ($n = 1$; Ohm's law) indicates the dominance of carbon black–carbon black contacts. A deviation from Ohm's law shows that the carbon black particles are separated by layers of the polymer.

In the presence of the tunnel effect, the dependence of the current on the potential is described by another expression:

$$i = Au^{n_1}e^{B/u},$$

where A, B, and n_1 are constants. It has been established experimentally that, with increase of the potential, this formula is suitable for the description of certain real systems starting from a critical potential[34]. However, one should note that the resistance may be Ohmic also in the presence of the tunnel effect. The characteristics of contacts of different types have been examined[35,36].

1. The Fluctuation Tunnelling Model

The fluctuation tunnelling model is apparently closest to reality[37]. According to this model, the conductivity of polymers filled with carbon black is determined by two factors. The ability of the carbon black to combine into chain structures (clusters) is responsible for charge transfer between the particles within the cluster directly via contacts. For certain relatively high degrees of filling, the distance between the clusters becomes much smaller than the dimensions of the latter and the conductivity is determined by the tunnelling of electrons between the clusters at the point of the maximum approach of the latter. Tunnelling is promoted by the thermal energy fluctuations (kT), which modulate the energy barrier; the decrease of the height of the energy barrier induced by the fluctuations can be fairly large. Furthermore, the presence of fluctuations leads to the appearance of a temperature dependence of the conductivity.

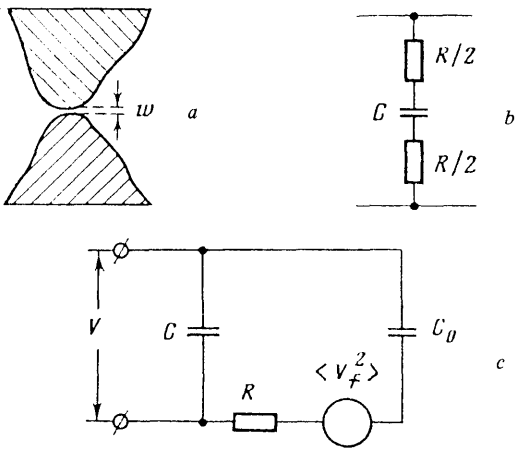


Figure 3. Equivalent circuit of the tunnel transition in the fluctuation tunnelling model[37]: *a*) type of contact; *b*) circuit; *c*) equivalent circuit (C_0 is the total capacitance between two particles).

Such a barrier can be represented approximately by a series-connected resistance R and a capacitance $C = S/4\pi w$ (where S is the area and w the distance between the clusters in the region of their maximum approach) and also by an equivalent circuit (Fig. 3). The fluctuations of the potential are described by the familiar Nyquist formula $\langle V_f \rangle^2 = 4kTRdf$, where df is the frequency range. Averaging with respect to the frequency and taking into account the equivalent circuit

yields the thermal fluctuations of the potential drop across the barrier $\langle V_T \rangle^2 = kT/C$.

Calculations yield the following temperature dependence of the resistivity of the composites:

$$\rho = \rho_0 \exp\left[\frac{T_1}{T + T_0}\right],$$

where T_1 is the temperature corresponding to the energy necessary for the electron jump across the gap between the clusters and T_0 is the temperature below which ρ is independent of temperature.

Experimental results have shown that composites based on poly(vinyl chloride) (PVC), filled with various types of carbon black, have conductivities whose temperature variation is described by the above formula[38]. This indicates the fluctuation mechanism of the conduction in the systems considered (Fig.4).

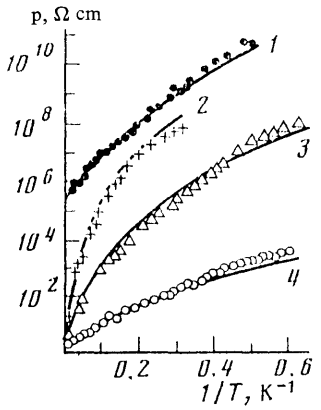


Figure 4. Temperature variation of ρ for carbon black-filled PVC compositions[38]: *1*) Mogul-L carbon black (45 wt.%); *2*) Columbia SA40-220 carbon black (15 wt.%); *3*) Columbia SA40-220 carbon black (20 wt.%); *4*) Ketjenblack EC carbon black (16 wt.%).

A characteristic feature of polymeric composites of this kind is that electrical breakdown occurs for comparatively low electric field strengths $E < 10^2$ V cm^{-1}. The low breakdown potentials are due to the fact that the potential drop occurs mainly in the gap between the conducting clusters and the gaps w are much smaller than the size of the cluster W. The field strength in the gap therefore reaches EW/w, which is sufficient for thermal breakdown[38].

2. The Degree of Linkage in Polymeric Composites

In order to estimate the degree of linkage between the particles of the electrically conducting filler in composites, one can apparently employ the approach developed for the determination of a measure of the degree of linkage of graphite[39]. The ratio of the electrical conductivity of the test specimen σ_m to the electrical conductivity of pore-free volumes σ_0, i.e. $K = \sigma_m/\sigma_0$, is used as a quantitative characteristic of the macrostructure of graphite. The quantity K varies from $K \cong 0$ for graphite powder to $K = 1$ for the single crystal. The conductivity σ_0 is determined from the concentration of the charge carriers n_0 and their mobility μ_0 by means of the formula $\sigma = en_0/\mu_0$. The quantity n_0 is usually close in magnitude to the concentration of carriers in the single crystal ($n_0 = 1.1 \times 10^{19}$ cm^{-3} at 300 K). This quantity can be determined by ESR. The following formula is used to determine μ_0:

$$\mu_0 = \frac{1}{H}\left[\frac{\rho(H) - \rho(0)}{\rho(0)}\right]^{1/4},$$

where H is the magnetic field and $\rho(H)$ the resistivity in the magnetic field.

We may note that K for different graphite specimens is linearly correlated with Young's modulus E, which in certain cases is determined solely by the degree of linkage in the specimen (Fig.5). The application of a similar approach to electrically conducting polymeric composites can yield information about the aggregation of the filler particles and the formation of conducting chain structures.

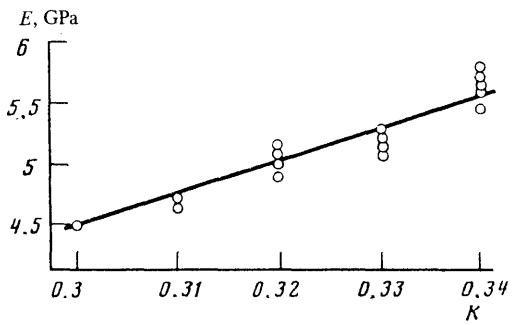


Figure 5. Dependence of Young's modulus E on the degree of linkage $K = \sigma_m/\sigma_0$ for graphite specimens[39].

3. The Percolation Theory

The most general approach to the description of the conductivity of non-ordered structures is apparently one involving the percolation theory[40,41]. Diffusion is usually regarded as the random movement of particles in an ordered medium; on the other hand, percolation is represented as directed movement in a non-ordered system. An example may be provided by the flow of water through porous minerals. Percolation in a regular lattice or in a continuous medium may be considered.

For a lattice made up of regularly distributed sites, where the neighbouring sites are connected by bonds, there is a possibility of, for example, flow of a current, a liquid, etc. between the sites. Disorder is introduced in two ways into such a system: (a) in a random fashion with a probability $1 - c$ by blocking (rupturing) the bonds in the system (the bond problem); (b) in a random fashion with a probability of $1 - c$ by blocking the sites (the site problem).

A macroscopically large (infinite) system is said to be permeable if the flow of a liquid (current, heat, etc.) through it via non-ruptured bonds (in case a) or similarly via bonds passing through non-blocked sites (in case b) is possible. The problem consists in the determination of the minimum value of c ($c = c^*$) down to which the infinite system remains permeable. The flow threshhold constitutes the threshhold of the formation of an infinite cluster of bonds "hooked" onto one another.

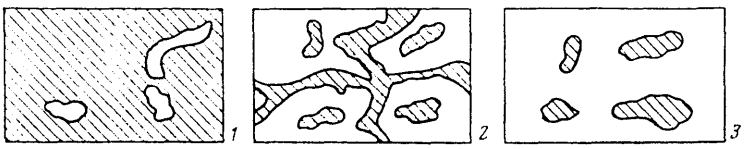


Figure 6. Dependence of the degree of linkage in a composite on the concentration of the conducting filler (shaded region) (c^* = percolation threshhold): 1) $c < c^*$; 2) $c = c^*$; 3) $c > 1 - c^*$.

If the distribution of conductivity in the material defined by $\sigma = 0$ with a probability $1 - c$ and $\sigma = \sigma_0$ with a probability c obtains, then, according to the percolation theory, the conducting parts of the material under conditions where $c < c^*$ are insulated from one another and the overall conductivity is zero. When $c \geq c^*$, a continuous conducting pathway appears through the entire specimen and the conductivity increases further with increase of c. Finally, when $c > 1 - c^*$, the non-conducting parts of the material are insulated from one another. Thus in the vicinity of the percolation threshhold c^*, there is an insulator–conductor transition, as shown in Fig.6.

More accurate results have also been obtained for binary continuous media[42], for which the local conductivity σ is equal to σ_0 with a probability c and to σ_1 with a probability $1 - c$, while $x = \sigma_1/\sigma_0 \ll 1$. The following relations have been obtained:

$$\sigma \sim \sigma_0 (c - c^*)^{\beta} \quad \text{when } c \gg c^*,$$
$$\sigma \sim \sigma_1 (c^* - c)^{-1} \quad \text{when } c \ll c^*,$$
$$\sigma \sim \sigma_0 x^{\delta} \quad \text{when } c \to c^*,$$

and $\delta = \beta/(\alpha + \beta)$. These relations are illustrated schematically in Fig.7.[42] The parameters for different problems of the percolation theory are presented below[42]:

	c^*	β	δ
Three-dimensional bond problem	0.25	1.6	0.67
Two-dimensional bond problem	0.48	1.1	0.51
Three-dimensional problem of percolation in a continuous medium	0.145	1.4	0.65
Three-dimensional model of a continuous (additive) medium	0.33	1	0.5

The model of an electrically conducting composite in which the filler particles are distributed at the sites of a regular three-dimensional lattice (cubic, diamond-like, etc.) has been examined[43]. It was assumed that the particles located at neighbouring sites are in contact. With increase of the filler concentration, the dimensions of the cluster consisting of particles in contact increase until a continuous chain passing from one edge to another is formed (i.e. the percolation threshhold is attained). In contrast to the traditional approaches of the percolation theory[40,41], this problem is solved by analogy with the problem of random motion in a three-dimensional lattice and resembles the model employed by Flory in the analysis of the conformations of polymeric chain molecules[44]. As a result, relations were obtained for different types of lattice between the average length of the continuous chain and the conductivity, on the one hand, and the filler concentration, on the other. The average percolation threshhold obtained[43] for six types of lattice was 0.095, which the author believes to be close to the value of 0.145 obtained by other methods[42].

An interesting example of a system of practical importance in which there is a dielectric–conductor transition of the percolation type is provided by the so-called granulated metals or cermets, which are composites consisting of a non-conducting matrix (SiO_2, Al_2O_3) in which fine grains of a metal (Ni, Pt, Au, etc.) are dispersed[8,45]. Such systems are used to prepare thick-film resistors.

The study of the dependence of the conductivities of such systems on the content of the metal c_M indicates the presence of three regions[45]. When $c_M < 0.4$, the system consists of insulated unconnected particles of the metal distributed in the dielectric matrix. In this case conductivity is due to the thermally activated tunnelling of charge carriers between the metallic particles. The transport of charge carriers takes place via electron "jumps" from one neutral grain to another; this results in the formation of a pair consisting of positively and negatively charged grains, which requires a definite consumption of energy. A characteristic temperature variation of the conductivity of the form $\sigma \propto e^{-A/\sqrt{T}}$ arises as a consequence[45].

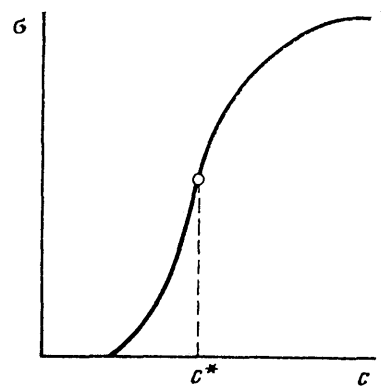


Figure 7. Dependence of the electrical conductivity σ on the concentration c_M of the conducting filler near the percolation threshhold for a two-component random medium.

In the region $0.4 < c_M < 0.5$ the percolation threshhold occurs; conducting chains permeating the entire specimen begin to be formed. When $c_M > 0.5$, the metal forms a continuous phase in which particles of the dielectric are distributed.

The high concentration of the metal corresponding to the percolation threshhold (50% of the filler instead of the theoretical value of 15%) is explained by the fact that, during the preparation of the cermets, layers of oxides preventing the transfer of electrons are formed on the surface of the metallic grains even when the particles are in contact. This shows that phenomena at the interface play an important role in the mechanism of conduction in composites. Indeed, when

$c_M > 0.5$ the resistivity varies in the following manner with the contact force between the particles:

$$\rho_c = 0.8\rho_M\left(\frac{E}{p}\right)^{1/3},$$

where ρ_M is the resistivity of the conducting phase, E the modulus of elasticity, and p the pressure in the system, equal to the ratio of the contact force to the area of contact[8].

Thus, in order to ensure electrical conduction, a simple contact between the particles of the conducting phase is insufficient—conditions ensuring an obstacle-free electron transfer between the particles are necessary.

4. Structured Composites

The so-called structured composites merit separate consideration. An example is provided by systems obtained by pressing mixtures of polyethylene or polypropylene and metal powders[10,11]. In this case the specimen is pressed at a temperature below the melting point of the polymer and the polymer particles do not therefore fuse and are merely deformed, while the metallic particles are distributed on the surface of polymer grains, forming a separate continuous two-dimensional phase. Such a structure is illustrated in Fig.2*B* (see structure 4). The dependence of the resistivity ρ_v on the content of the metal is illustrated schematically in Fig.8. Evidently, up to a concentration c_A, the conductivity varies little—a continuous filler phase is not formed. From the instant of the formation of the continuous phase, the resistivity falls sharply but, at a concentration in excess of c_B, the decrease slows down.

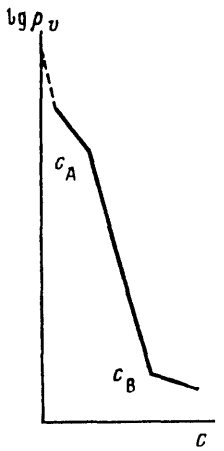


Figure 8. Schematic illustration of the dependence of ρ_v for the polyethylene–nickel composite on the nickel concentration[10].

The degree of filling c_B corresponds to the case where a close-packed layer of metallic particles is formed on the surface of each grain, i.e. N_p polymer spheres with a radius R_p are coated by N_M metallic spheres with a radius R_M:

$$N_p \times 4\pi R_p^2 = N_M\, \pi R_M^2 \Phi\,,$$

where Φ is a coefficient which depends on the type of packing.

When $c > c_A$, the layers of filler particles are built up and the conductivity increases slightly, approaching the conductivity of the filler. The quantity c_B is calculated from the formula

$$c_B = \frac{\frac{4}{3}\pi N_M R_M^3}{\frac{4}{3}\pi N_M R_M^3 + \frac{4}{3}\pi N_p R_p^3} = \frac{1}{1 + \frac{\Phi}{4}\cdot\frac{R_p}{R_M}}\,.$$

When $c_A = \frac{1}{2}(P_c c_B)$, the two-dimensional metallic phase is a monolayer (P_c is the packing coefficient).

The packing coefficients Φ and P_c for different types of lattice are as follows in the case of a structured composite:

	Hexagonal lattice	Cubic lattice	Trigonal lattice
Φ	1.11	1.27	1.375
P_c	1/3	1/2	2/3

It is noteworthy that the transition c_A for structured composites corresponds to much lower degrees of filling than for a statistical mixture. Comparison of the experimental and theoretical results for the dependence of the percolation threshholds c_A on the ratio of the particle radii R_P/R_M for a structured composite is indicated below:

R_P/R_M	30	16	12	10	7.5
c_A (theor.)	2.9	5.1	6.5	7.5	9
c_A (exp.)	6	6	11	13	14

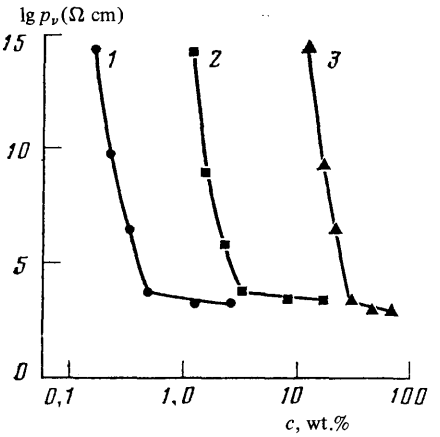


Figure 9. Dependence of ρ_v on the concentration c of the Ketjenblack EC carbon black for different methods of preparation of polymeric composites based on polystyrene[46] (see text).

IV. METHODS FOR THE PREPARATION OF COMPOSITES AND THEIR ELECTRICAL CONDUCTIVITIES

The examples quoted above show that the method of preparation of the composites is important for the attainment of a specific electrical conductivity. Shear forces, which should be maximum in the stage where the composite is prepared and minimum in the stage involving the formation of articles from it, play an important role here. The temperature and mixing time of the components, the order in which they are introduced, the presence of substances altering the viscosity of the mixture, etc. have a significant influence on the conductivities of composites[3,10].

This can be illustrated by several further examples. The dependence of ρ_V for the polystyrene–Ketjenblack EC carbon black composites on the carbon black concentration has been investigated[46] for different methods of preparation of the composite. Three mixing procedures were used: (1) pressing of a mixture of carbon black with the powdered polymer; (2) mixing of the carbon black with a solution of the polymer in toluene in a ball mill followed by the casting of a film with slow evaporation of the solvent, comminution of the film, and pressing; (3) calendering of a mixture of carbon black and the polymer between heated rollers, grinding of the product, and pressing. Fig. 9 shows that the critical concentration of the carbon black c_B for the first method is only 0.5%; evidently this case is close to the model described above with $R_P/R_M \gg 1$. For the third method, c_B increases to 25%. In this procedure it is apparently more difficult to retain the conducting carbon black structure.

Certain carbon black-filled compositions are used to prepare articles by extrusion. Thus the RCA Company (USA) uses the propylene–vinyl chloride copolymer–Ketjenblack EC carbon black composition to manufacture video discs for the recording of television programmes[47]. Fig. 10 illustrates the dependence of ρ_V for such a composition (measured using d.c. and a.c.) on the number of extrusions n. Evidently the optimum conducting structure is formed when $n = 2$; after a larger number of extrusions, the structure breaks down.

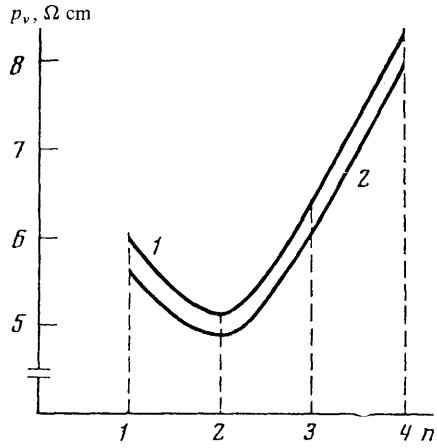


Figure 10. Dependence of ρ_V for the composition comprising the propylene–vinyl chloride copolymer and the Ketjenblack EC carbon black on the number of extrusions[47]: *1*) $f = 0$; *2*) $f = 9.5$ MHz.

Surfactants are used to improve the dispersion of the carbon black in polymers. Binary fillers are also employed. Thus, when 110 parts of kaolin are added to the ED-16 epoxide resin containing 10 parts of graphite per 100 parts of the resin, the ρ_V of the composition diminishes by six orders of magnitude (from 10^9 to 10^3 Ω m). In the absence of kaolin, the same value of ρ_V can be obtained only after the introduction of 50 parts of graphite. The effect of kaolin is explained by the fact that it promotes a rigid fixation of the electrically conducting structures which determine the stability of the electrical properties of the filled material[48,49].

In the preparation of electrically conducting films from pyrolysed polymers on the surfaces of inert fillers (kaolin, talc, etc.), there is a possibility of obtaining compositions based on these fillers and polyethylene and with a low content of the conducting component for which ρ_V is smaller by 5–11 orders of magnitude than the value for the initial polymer. The content of the conducting component (pyrolysed polyacrylonitrile) is then only 1–3%.[50]

A new method for the preparation of filled polymeric materials—the method of polymerisation filling—has been developed recently[18,19,41]. In this procedure the catalyst is deposited on the surface of the filler where polymerisation takes place. The resulting material can then be converted into articles by the usual methods. Polypropylene–graphite compositions have been obtained by this procedure; for comparison, the same compositions were prepared by extrusion[20] and it was found that the films of the polymerisation filled polymers have a much smaller resistivity ρ_V (by 2–8 orders of magnitude) than the extruded films with the same graphite content. A specific instance of the interaction of the filler and polymer apparently occurs here, which leads to the cleavage of the graphite along its planes and its more effective dispersion in the polymer. The details of this process are in the research stage, but many results support this hypothesis.

In conclusion one should mention organic polymers which are as it were "intrinsic" composites. Their electrical, optical, and certain other characteristics indicate the presence of conducting regions in a non-conducting matrix of the same composition. Among such systems, mention may be made of pyrolysed polymers (polyacrylonitrile, polyimides[38]) as well as doped polyacetylene[51,52].

V. APPLICATIONS OF CONDUCTING COMPOSITES

The range of applications of conducting composites is extremely wide. New possibilities for their employment are nowadays discussed in the literature, in particular in meeting the requirements of radioelectronics for the creation of low-noise and high-frequency cables and shields over a wide frequency range, in components of radioelectronic apparatus, in highly efficient solar batteries, and in other fields[7,53,54].

The employment of capacitive transducers for the decoding of information from video discs require the creation of compositions with a high degree of homogeneity in the distribution of the filler in the matrix and with reproducible properties. The Ketjenblack EC composition[47] mentioned above satisfies such requirements.

Among other potential applications of such composites are those in the chemical industry and non-ferrous metallurgy where there is a need to replace the scarce lead and leaded steel employed in the manufacture of electrofilters[55,56]. Composites with a level of conductivity not less than 10^{-6} Ω^{-1} cm^{-1} are widely used as antistatic materials[3].

A tendency has arisen in recent years to employ highly filled composites incorporating carbon fibre fabrics in electrical engineering for the manufacture of collectors and contact rings in electrical machines[57,58]. The comparatively small-scale application of conducting composites in the preparation of tensotransducers, necessary both in the modelling and employment of constructional equipment, is no less important[59].

As already stated, the creation of highly conducting polymeric adhesives constitutes an urgent task, since hitherto they have been made from scarce noble metals (Au, Ag, etc.)[9].

Vigorous studies are being prosecuted nowadays in order to prepare conducting composites with the aid of new methods—polymerisation filling[20,60], electrochemical deposition of metals from salt solutions into a polymer solution[12,57], and high-speed thermal decomposition of solutions of the metal carbonyls, formates, and oxalates in polymers[14]. This factor gives rise to the hope for the creation of new composites with a set of new valuable properties[61,62].

* * *

One of the main difficulties in the study of the electrical conductivities of organic, including polymeric, materials is that they cannot be treated within the framework of classical ideas, for example, within the framework of the band model. A criterion of the applicability of this model is a current carrier mobility $\mu > 1\ cm^2\ V^{-1}\ s^{-1}$. For the majority of the electrically conducting polymers in composites, this condition is [not?] fulfilled: thus $\mu \cong 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$ for carbon black-filled raw rubbers[34]. Another factor which hinders the understanding of the mechanism of electrical conduction in composites (for example, those based on polyolefins) is that the concentration of the intrinsic current carriers in polymers of this class is negligible. Thus the conducting properties of such composites are determined, firstly, by the material of the filler and secondly, by the properties of the filler–polymer interface. Since the electrical conductivity is ensured by carriers injected from the filler, it is necessary to create interphase injecting contacts (ohmic contacts are suitable in some cases).

Thus, in order to understand the mechanism of the electrical conduction in polymeric composites, it is necessary to take into account the influence of a number of factors, which include the properties of the filler and the polymer, the distribution of the filler in the matrix, and the type of contacts between the polymer and the filler particles. None of the models existing at the present time takes into account all these factors and reflect only one of the characteristic aspects of the phenomenon. In view of the increasing use of such composites, it is therefore necessary to carry out combined theoretical and experimental studies on the lines discussed above.

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Metallic Clusters in Polymer Matrices

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The methods of synthesis, the properties, and the structure of new composite materials based on polymers and on clusters of the transition metals are discussed. The properties of metal-polymer systems of this type are shown to be very different from those of ordinary metal-polymer systems, in which the metal particle size is greater than 100 μm. The effect of the clusters on the structure of the polymers is examined, and examples of the dependence of the electrophysical and magnetic properties of metal-polymers on the concentration of metallic clusters are given. 62 references.

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I. INTRODUCTION

Exploratory research on new types of material based on polymers for use in electronics has been intensified in the last few years both within and outside the Soviet Union. The outcome of much of this work has been polyconjugated polymers, such as polyacetyl, polyphenylene, polydiactylene, polypyrrole, etc.[1-3] Being dielectrics with a wide forbidden gap in the energy spectrum of their charge carriers these materials can be doped with electron acceptors (such as halogens, or arsenic or antimony pentafluorides) to give organic semiconductors and organic metals whose electrophysical parameters can be controlled between wide limits.

However, these polymeric materials are still far from being generally available, for a number of reasons, including the lack of large-scale methods of preparation of the initial polyconjugated polymers. We have therefore turned our attention towards the familiar and readily available polymers polyethylene and Teflon. The controlled addition of dopants of different chemical nature (both donors and acceptors) to these materials had be developed. Since the introduction of metal particles of various sizes into this type of polymer matrix had already been demonstrated, we initialy used clusters of the transition metals as dopants.

The expectation that this modification of polyethylene and Teflon could lead to new materials with interesting electrophysical properties was stimulated by a series of papers by Enikolopyan and co-workers[4,5], who showed that the injection mechanism of electrical conduction (which they had observed at high pressures) can be realised at ordinary pressures if the integration of metal and the polymer can be carried out at the "molecular level".

In this review we shall examine the methods of preparing single-phase metal–polymer composites from the inert polymer matrices Teflon and polyethylene (not containing multiple bonds) doped with metal particles of size comparable to the thickness of a single polymer chain. By this approach we have produced a new type of material (which we have termed "cluspols") in which metal clusters are accommodated within the natural cavities of the polymer matrix[6].

II. METHOD OF PREPARING METAL–POLYMERS

Industrial methods of preparing metal–polymer composites usually rely on metal powders (of fairly large particle size), which are added to a melt of the polymer with stirring. However, this method cannot give a uniform distribution of particles in the polymer, and furthermore it tends to degrade the stability characteristics of the composite.

Several alternative methods of preparing metal–polymers have been described: we shall examine some of them in detail.

1) The electrochemical reduction of metals from solutions in the presence of surface-active substances (SAS).[7-11] Polymers containing functional groups can play the role of the SAS. It has been shown[12] that even when the amount of active filler is very small its particles act as centres for the formation of a continuous three-dimensional network through the adsorption and orientation of the polymer molecules under the influence of the field of force of the filler particles. The influence of various factors on the current yield and on the dispersion of the metallic filler has been studied in detail[13-15]. The electro-flotation[16] and the electro-acoustic method[17] are variants of the electrochemical method of synthesis of metal–polymers.

2) The mechanochemical method of synthesis of metal–polymers[18,19] relies on the high adsorption and chemisorption activity of the surface created during the dispersion of a metal. Polymerisation processes during the vibratory milling of salts, metals, and oxides in the presence of vinyl monomers have been studied, and chemical grafting of the metallic particles to the polymer surface was observed during the milling of iron, nickel, titanium, and chromium.

It was reported[20] that the absence of reactive functional groups in the polymer affects the physicochemical properties of the polymer: for example, grinding finely divided iron with polyethylene (even in large excess) does not form a metal–polymer. Furthermore, the main properties of the resulting composite are strongly dependent on the dispersion conditions, and on the shape of the metal particles. Optimising the dispersion time is equally important, since excessively long mechanical treatment of the polymer system may cause mechanical degradation[21]. Thus the mechanical method of synthesis of metal–polymers is applicable mainly to polymers which contain functional groups or multiple bonds, and which can therefore generate chemisorptive interactions between the polymer molecules and the surface of the metal particles[22,23].

3) The displacement method depends on the fact that in the presence of polymers metals can be displaced from salt solutions and form metal–polymers if the electronegativity of the matrix is high enough. This method does not appear to have been widely used: the few papers which refer to it are reviewed in Ref.24.

4) The thermal method of metal–polymer synthesis is the most widespread at the moment[25–28]. It relies on the tendency of the slats of organic acids (formates, oxalates, etc.) and of many metal–organic compounds (MOC) to dissociate into the metal (or metal oxide) and give a volatile compound when heated. Thermoplastic polymers can be used as the organic host material for the decomposition of MOC, giving metal-filled composites as the reaction product.

Unlike the usual mechanical mixtures of polymers and metals, in metal–polymers prepared by the thermal method, the metal particles have a fairly high dispersion, they are evenly distributed through the bulk of the polymer, and the sorption of the macromolecules on their surface is strong and irreversible[29–36].

5) The plasmochemical method. Metal-containing composite materials have been prepared[37] by a high-frequency plasma technique in which the polymerisation process was carried out within the plasma chamber. Two methods of transferring the metal to the gas phase before incorporating it in the growing polymer have been proposed: evaporation of the metal (tin) in an inert gas atmosphere and decomposition in the plasma of a volatile compound of the metal [for example, $Cr(CO)_6$]. The products were analysed by the ESCA method, and it was found that the technique can produce highly dispersed metallic particles in a polymer, covering a wide range of metal–polymer compositions. It was also found that the metal particle size depends on the properties of the polymer: for example, in C_2H_4 the size of Sn particles was 150 Å, in C_6H_4 the size of Cr particles was 500–700 Å, and in C_2F_4 the size of Cr particles was 3000 Å.

Though this method seems very promising for the preparation of metal-containing polymers it does not appear to have been used for this purpose.

6) Cryochemical methods of synthesis of metal-containing polymers[38] are potentially very useful. They rely on the fast diffusion of metal vapours towards a cooled surface covered with a thin layer of polymer. Alternatively, the reaction is carried out in a rotating reactor, and the metal–polymer composite is obtained in the bulb of the rotating apparatus. Francis and co-workers[39,40] prepared metal-containing polymers of the poly(methyl phenyl siloxane) type (DC-150) and studied their u.v. spectra. Various metals (titanium, chromium, molybdenum, vanadium, and tungsten) were used as fillers. It was shown that at low concentrations of the metal in the polymer the metallic clusters are coordinated to the phenyl groups of the polymer to give compounds of the *bis*-arene type. Monatomic, diatomic, and triatomic metal clusters, both single and bimetallic (Cr_xTi_y, etc.) were obtained[40] in a matrix of poly(methyl phenyl siloxane). However, the metal–polymer composites thus obtained were found to be unstable if the temperature was allowed to rise to 25 °C or if the concentration of metal was increased.

Thus, in spite of the many methods of synthesis of metal–polymers already disclosed, new methods are needed for the preparation of materials stable under normal conditions and containing a narrow distribution of particle sizes in the range of 15–50 Å.

1. Effect of Dispersed Fillers on the Properties and Structure of Polymers

Let us examine more closely the structure of the polymer molecules, and calculate the effect of the introduction of relatively coarse metallic filler particles on some of the properties of the polymers.

The structure of polymers is characterised by crystalline regions (blocks, or stacks) randomly distributed within the amorphous mass. Orientational ordering of the crystalline fragments can be obtained by stretching or rolling the polymer[41].

The insertion of even relatively small metal particles (~250 Å) should cause substantial disruption of the polymer structure: in practice, the metal particles in metal–polymers are several orders of magnitude larger, and their influence on the polymer structure is correspondingly more marked.

The presence of metallic fillers of ordinary particle size (1–5 μm) can produce some specific properties in polymer materials (for example, enhanced thermal and electrical conductivity, higher magnetic susceptibility and specific heat, and resistance to ionising radiation). However, usefully large changes in properties are achieved only at high concentrations of the metallic filler[42]. Thus, in nickel–polyethylene composites the required electrical conductivity (5.8×10^3 Ohm^{-1} m^{-1}) could be achieved only at a concentration of metallic particles greater than 50 vol.% (90 wt.%). According to current views, the highest conductivity is observed when a substantial fraction of the sample volume is occupied by connected chains of electrically conducting particles with a cross-section equal to the area of contact of the particles. This type of material has only limited applications in technology because its properties cannot be optimised.

In the electrical conductivity scale of materials the extreme positions are occupied on the one hand by typical insulators such as Teflon and polyethylene, and on the other hand by typical metals such as copper and silver. The conductivity can be increased by 5–14 orders of magnitude in some materials by doping[1]. The doping (a special type of alloying) usually involves placing particles of the doping element in vacancies of the crystal lattice of the host material. The two types of particle should be comparable in size. From this formal analogy we can expect the doping of polyethylene or Teflon with metals to bring their conductivity into the typical semiconductor range.

Thus the problem of controlling the electrophysical properties of Teflon or polyethylene reduces to introducing into these polymer matrices dopants comparable in size to the vacancies (or holes) in the initial polymer.

Let us consider once again the structure of the polymer matrices. Polyethylene and Teflon are typical semi-crystalline polymers, with a crystallinity of 60–85% and 75–80% respectively. The molecules in the polymer chain form a planar zig-zag structure with an angle of 112° between the units. In the case of polyethylene the self-repeating unit consists of two CH_2 groups. The polytetrafluoro-ethylene molecule has a more complex zig-zag structure because of the fairly large size of the fluorine atoms[43].

The crystalline part of the polymer structure usually consists of platelets 10–20 μm wide and ~100 Å thick. The main axes of the chains are found to lie at right angles to the plane of the platelets. The thickness of the platelets is much smaller than the chain length. Thus one molecule of polyethylene (with a mass of 50000 and a length of 4500 Å, say) repeatedly crosses the boundaries between crystalline and amorphous regions. Even the crystalline parts of the polymer contain a large number of holes (or defects): these include stacking faults, irregular arrangement of tapes, plates, etc., and therefore the microcrystallites in polymers are usually treated as formations with a high concentration of defects[44].

The amorphous regions in the polymer structure are even "looser", and contain a larger number of natural "holes": the bond between the chains is weaker than in the crystalline blocks, giving greater mobility to the amorphous segments of the molecules.

2. Method of Synthesis of Composite Materials of the "Cluspol" Type

We shall now consider the methods of forming metallic clusters in the natural holes of polymeric matrices by the fast monomolecular thermal decomposition of solutions of metal compounds in a melt of the polymer.

According to modern views, melts of polymers consist of distinct spherulites which retain (in a slightly distorted form) the original platelets or lamellae as unchanged constituents. In other words, the melt retains the short-range order of the initial polymer structure, but the pre-existing holes become accessible for the insertion of metallic particles[45].

The thermal decomposition of metal compounds has been studied widely, under various conditions. In some cases it was shown to be a good method of preparing highly dispersed and very pure metal particles[46]. An overall scheme of thermal decomposition with formation of volatile ligands and a "hot" metal atom M* is given below. The cluster of metal atoms M_n which begins to grow in the melt is stabilised in the polymer matrix. A specific example [the thermal decomposition of $Fe(CO)_5$] is also given.

$$ML_n \rightarrow M^* + nL$$
$$mM^* \rightarrow [M]_m \text{ (cluster)}$$
$$Fe(CO)_5 \rightarrow Fe + 5CO$$
$$\Delta G_{400K} = -8.98 \text{ kcal mole}^{-1}; \Delta G_{600K} = -36.82 \text{ kcal mole}^{-1};$$
$$\Delta G_{1000K} = -92.50 \text{ kcal mole}^{-1}$$
$$15Fe + 4CO \rightarrow Fe_3O_4 + 4Fe_3C$$
$$Fe_3O_4 + 6CO \rightarrow Fe_3C + 5CO_2$$
$$CO \rightleftarrows 0.5CO_2 + 0.5C$$

It is found that an increase in temperature causes an increase in the extent of decomposition of the carbonyl by the main reaction, and correspondingly lowers the yield of side-products[47].

In some recent work the thermal decomposition of metal carbonyls has been used as a source of pure metals (polymer fillers). Thus the preparation of zero-valent iron by the thermal decomposition of $Fe(CO)_5$ in a solution of "functional" polymers has been described[27,48]. It was shown that polymers containing functional groups act as catalysts for the thermal decomposition of $Fe(CO)_5$ to iron(0) through an intermediate of the butadienyl–$Fe(CO)_3$ type, whereas in polymers without functional groups the thermal decomposition goes through the disproportionation of $Fe(CO)_5$. The average size of the iron particles in the composites was ~70–80 Å.

Ultra-dispersed particles of Fe_2O_3 were obtained[49–51] by thermal decomposition of $Fe(CO)_5$ under oxidising conditions in polymers not containing functional groups (polyethylene, polytetrafluoro-ethylene, polypropylene). The preparative method consists in the adsorption of $Fe(CO)_5$ on the surface and in the bulk of the polymers, followed by thermal oxidation at 105 °C in air. The value of this method in the preparation of stable composites of iron(III) oxide and polymers was convincingly demonstrated. The average size of the Fe_2O_3 particles was 30–80 Å.

For the reasons mentioned above the formation of metallic clusters in a polymer melt was carried out at the highest permissible melt temperature, well in excess of the incipient thermal decomposition temperature of the compound. Additional requirements included the highest possible dilution of the solution of metal-containing compound in the thermal decomposition step and the fastest and fullest possible removal of the volatile ligands from the reaction mixture. The proposed method was tested with several types of polymer and different metal compounds (iron, cobalt, molybdenum, and chromium carbonyls, π-allyl compounds of the platinum metals, and acetates, formates, and other metal compounds)[5]. The metal–polymer materials prepared in this way can easily be shaped by moulding. The products included films of high-pressure polyethylene HPPE + M (where M = Fe, Cr, Ni, Cu) prepared at 125 °C and 150 atm, and sheets and rods of polytetrafluoro-ethylene PTFE-40 + Fe prepared at ~280 °C and 150 atm.

The method has been repeatedly shown to be applicable to a wide range of polymer matrices with different types of compounds and different metals, as well as metallic mixtures, alloys, oxides, sulphides, etc. The resulting powders can be formed into articles of any shape by standard methods. Thus we have developed a method of producing a new type of material for which the technical term "cluspol" has been proposed.

The detailed structural features of these materials, including the distribution of the metal particles, their state of oxidation, interactions with the polymer matrix, etc. were studied by a wide range of physicochemical and analytical methods (DTA, X-ray phase analysis, low-angle X-ray diffraction, i.r. spectroscopy, NMR spectroscopy, and Mössbauer spectroscopy).

On the whole, the most sustained and detailed studies were made on high-pressure polyethylene and Teflon-40 containing iron clusters. Samples containing other metals or other matrices received only occasional study.

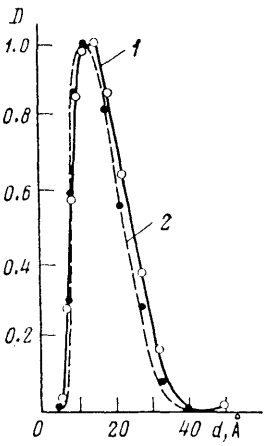


Figure 1. Size distribution of chromium clusters in a Teflon-40 matrix containing 1.0 (*1*) and 5.0 wt.% of Cr (*2*).

III. STRUCTURE AND PHYSICOCHEMICAL PROPERTIES

1. X-Ray and Mössbauer Studies of Metallic Clusters in Polymer Matrices

Metal lines cannot be detected by X-ray phase analysis in "cluspol" materials until the concentration of metal exceeds 10%. Samples containing less than 10% of metal were studied by the low-angle X-ray diffraction method[6]. A typical distribution is shown in Fig.1. Chromium in Teflon-40 gave a particle size distribution curve with a single narrow maximum at $d \cong 12.1$ Å. In the case of iron clusters in a polyethylene matrix the picture is more complex: at low concentrations we again find a narrow distribution with a maximum at 14.8 Å,

but at higher iron concentrations a second, flat maximum appears in the curve at $d \cong 70$ Å (Fig.2). A further increase in the concentration of metal in the material shifts the peak towards larger cluster sizes, but even in this case more than 80% of the clusters have a diameter smaller than 40 Å.[6]

The low-angle X-ray diffraction method can be used to determine the periodicity of the distribution of clusters in the matrix: typical results[6] for iron clusters in polyethylene are shown in Table 1. We note that at high concentrations the average distance between clusters is not more than two or three cluster diameters. The size of the iron clusters was determined by the static magnetic susceptibility method. From the plots (Fig.3*b*) of the specific magnetisation against temeprature for different iron concentrations we note that the downward slope is steeper than for massive iron (which has a Curie temperature of ~1000 K). A size dependence of the Curie temeprature cannot be excluded for very small particles.

Table 1. Periodicity (l) of the distribution of iron clusters in high-pressure polyethylene[6].

[Fe], wt.%	l, Å	[Fe], wt.%	l, Å
1.10	315±30	8.08	110±5
2.64	220±12	29.6	90±5

By measuring magnetisation in small fields the size of the iron clusters in the polymer matrix was determined on the assumption that the separate clusters display supermagnetism[52]. We know that the number of iron atoms (n) in a superparamagnetic particle, its volume (V), and its size (r) can all be determined from the initial slope of the experimental magnetisation curve:

$$n=\mu/2.2\ \mu_B;\ V=nM_B(\mathrm{Fe})/N_A\rho$$

where μ is the magnetic moment of the superparamagnetic particles, $2.2\mu_B$ is the magnetic moment of the Fe atom, and ρ is the density. We note from Fig.3*a* that the initial linear portion is most developed in the sample with an iron concentration of 3 wt.%. For this composition the following results were obtained: $n = 286$, $V = 3401$ Å^3, and $r = 15.1$ Å. The deviation from linearity arises because of the presence (in addition to the main group of supermagnetic particles ~15 Å in size) of a smaller number of larger particles which contribute ~5% to the toal magnetisation. These results are fully consistent with those obtained by low-angle diffraction on the same samples.

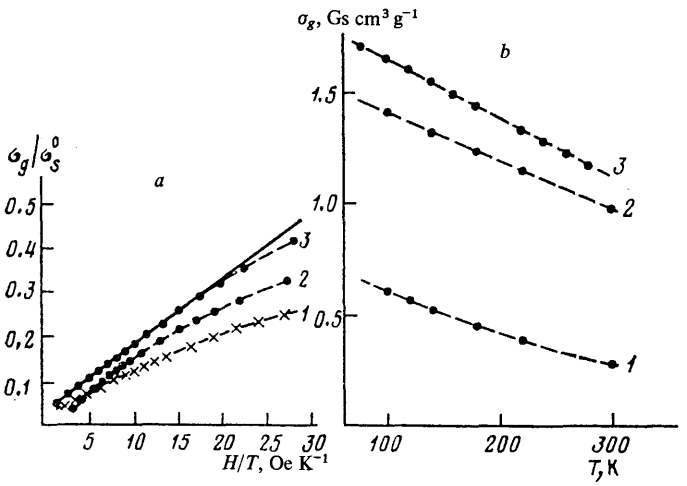


Figure 3. (*a*) Plot of the ratio σ_g/σ_s^0 (where σ_s^0 is the saturation magnetisation at 0 K) against H/T, and (*b*) temperature dependence of the specific magnetisation σ_g, for samples of polyethylene with different iron content: *1*) 1.0, *2*) 2.0, *3*) 3.0 wt.%.

The presence of iron clusters in these materials is confirmed by the Mössbauer spectra of "cluspol" samples. In the typical spectra shown in Fig.4 the main component at 300 K is a doublet with a quadrupole splitting of 0.6–0.9 mm s^{-1} and an isomeric shift of 0.6–0.7 mm s^{-1}. The parameters of the spectrum differ from the values for both α and γ

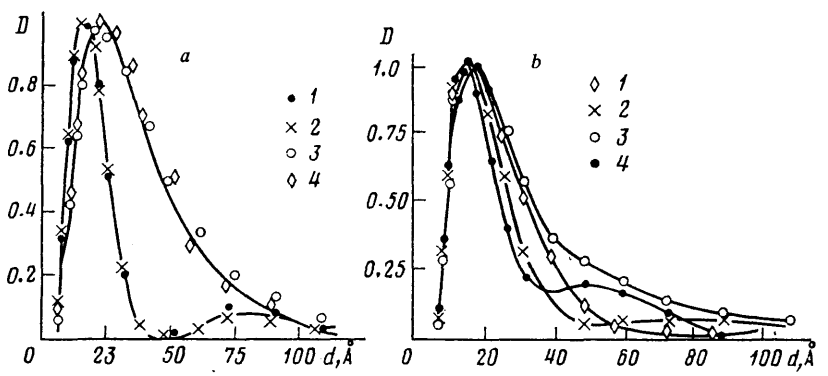


Figure 2. Size distribution of iron clusters in a high-pressure polyethylene matrix (*a*) and in Teflon (*b*); Fe content of the HPPE matrix: *1*) 0.7, *2*) 1.0, *3*) 5.0, *4*) 7.0 wt.%; Fe content of Teflon; *1*) 1.0, *2*) 5.0, *3*) 25.6, *4*) 10.0 wt.%.

iron (whether massive or in thin-film form)[55,54], and they agree with the parameters of the Mössbauer spectra of iron clusters in an argon matrix[55].

Thus the available data convincingly show that the proposed method gives metallic clusters with a narrow size distribution, and that these clusters are stabilised in the polymer matrix.

2. Effect of Metallic Clusters on Polymer Structure: NMR Studies

The nature of the interaction between metallic clusters and the polymer matrix, and the resulting changes in the matrix, were studied by NMR. The NMR spectra of the initial polyethylene samples are symmetrical, and consist of a broad and a narrow component (Fig.5). The narrow component is associated with the amorphous part of the polymer, the broad component with the crystalline part. An increase in the concentration of metallic clusters produces marked changes in the NMR spectra. Initially the intensity and the width of the narrow component are affected, but at higher concentrations the broad component begins to expand rapidly and beyond a certain metal concentration the NMR spectrum can no longer be measured[56].

Both the crystalline and the amorphous regions of the polymer can act as localisation sites for the clusters. The processes by which the metal particles are incorporated into the polymer can be monitored by analysing the NMR spectra.

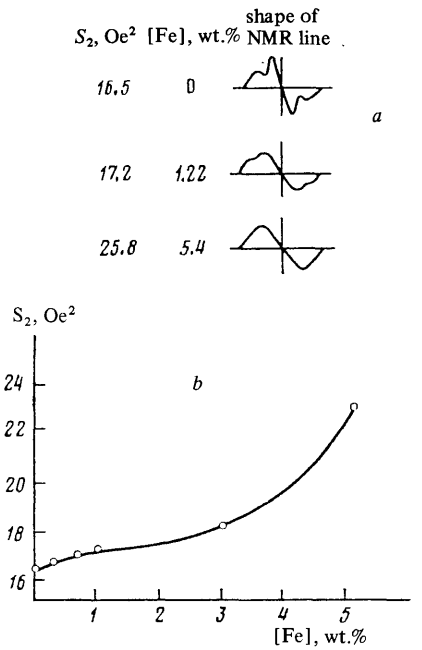


Figure 5. Effect of increasing the iron content on the shape of the NMR line (*a*) and on the value of the second moment S_2 (*b*) for composite polymers based on polyethylene.

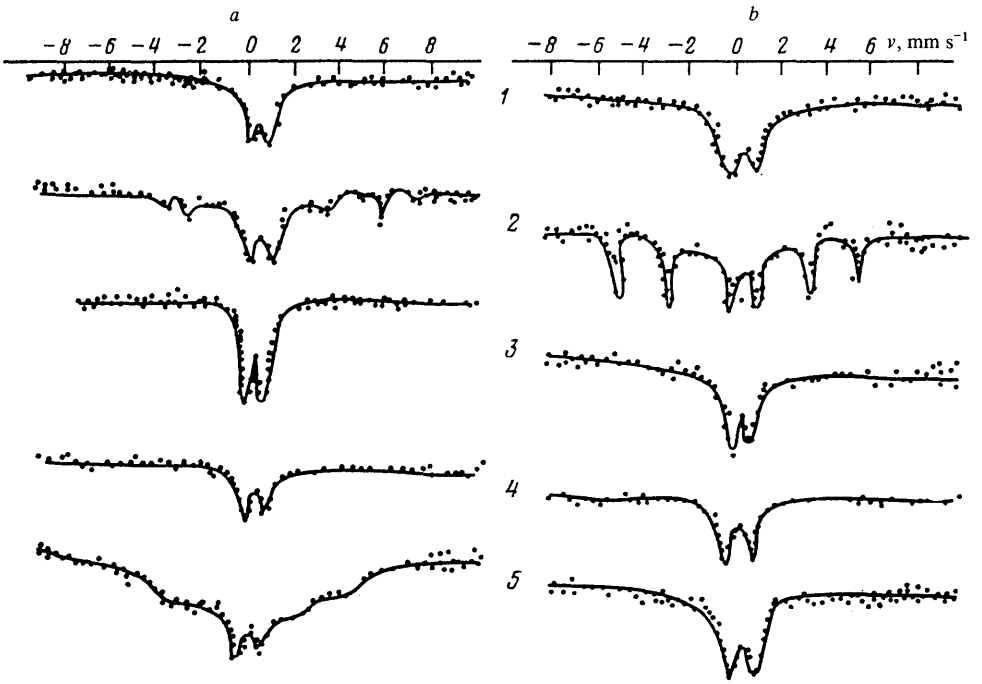


Figure 4. Mössbauer spectra of "cluspol" materials: (*a*) PE + Fe, (*b*) PTFE + Fe. Metal concentration: *1*) 3.0, *2*) 5.0, *3*) 7.0, *4*) 10.0, *5*) 30.0 wt.%.

Thus, as we have already pointed out, the narrow component is the first to be affected in the PE spectrum. Since the NMR spectra give information on the mobility of molecular chains, the decrease in intensity and increase in width of this component indicate changes in the segmental motion of the molecular chains in the amorphous phase, and also in the rotational and diffusive motions of the CH_2 groups about the fixed axes[57]. Thus the NMR results confirm that the formation of metallic particles begins in the amorphous regions, which are "looser" than the crystalline regions.

The introduction of metallic clusters makes the material more monolithic (more "pseudo-crystalline"), and also more thermally stable.

Table 2. Effect of the presence of iron clusters on the melting points of composites.

Sample	[Fe], wt.%	T_f, °C	Sample	[Fe], wt.%	T_f, °C
PP (atact.)*	0	89.0	PP (atact.)	30	155.0
PP (atact.)	3	123.0	PP* (isotact.)	0	158.0
PP (atact.)	5	145.0	PP (isotact.)	5	166.0

*Sample heated and treated in the same way as in the preparation of "cluspols" except for the addition of the MOC.

Direct experimental measurements of the thermal stability of the polymers (Fig.6) show that the addition of small amounts of metal raises T_{dec} by 50–80 K. More interesting results were obtained with atactic polypropylene (PP), which is a waxy substance with a softening temperature of ~90 °C. The addition of even very small amounts of iron to this material causes a sharp rise in the melting point, which can be made to approach the melting point of isotactic polypropylene (Table 2).

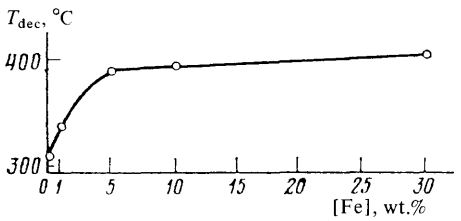


Figure 6. Effect of the addition of iron clusters on the thermal stability T_{dec} of polyethylene.

Since thermal stability is often related to molecular mobility, we should examine the dynamics of the polymer chains. The temperature dependence of the spin–lattice relaxation time (T_1) of the protons has been studied in a sample of LPPE (low-pressure polyethylene) containing ~30 wt.% of iron (particle size ~20 Å). Temperature plots of the spin–lattice relaxation times in the initial PE and in LPPE + 30% Fe are shown in Fig.7. This behaviour of T_1 reflects an average of the molecular mobility characteristics of the two phases (crystalline, and amorphous). The minima at 260 and 280 K for PE and PE + 30% Fe respectively can obviously be ascribed to the segmental motion of the polymer chains, whose thermodynamic characteristics tend to describe the thermal stability of the PE. In the temperature region of the minima in T_1 the correlation frequency (ν_c) of the molecular motion is equal to the spin precession frequency ν_0 (~40 MHz). The depth of the relaxation minimum in this case is a measure of the amplitude of the segmental motion of the polymer chain elements as well as of the change in the relative amount of the phases with different molecular mobility.

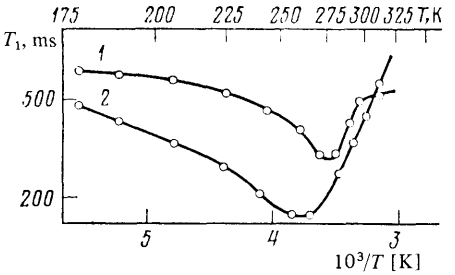


Figure 7. Temperature dependence of the spin–lattice relaxation time in the initial polyethylene and in polyethylene containing 30 wt.% of iron: *1*) initial LPPE, *2*) LPPE + 30%.

Thus the shift of the relaxation minimum in the high-temperature region of PE + 30% Fe, and the increase in T_1, denote the same effect: a strongly hindered segmental motion (as compared with the initial PE), and a correspondingly lower displacement amplitude. Since the amorphous phase has a higher molecular mobility, the motion of the polymer chains is suppressed in this phase at first, and the thermodynamic characteristics change towards those of the crystalline phase. However, conversion of the amorphous phase into a crystalline phase by the addition of finely divided iron seems unlikely. More probably, the very small iron particles are deposited initially in the amorphous, looser regions of the PE sample, where they suppress the molecular motions both by decreasing the free volume and (possibly) by forming chemical bonds with the matrix. This process, which increases the thermal stability, should be accompanied by changes in all the spectral characteristics, including the spin–lattice relaxation time, the specific heat, and the mechanical properties at ordinary temperatures.

Very surprising results were obtained by comparing the melt-flow indices of polyethylene and polyethylene with 20% of iron: the average flow decreased from 6.12 g to 0.049 g, i.e. more than 100-fold.

3. Some Physicochemical Properties of Materials of the "Cluspol" Type

The polymer matrices (polyethylene and Teflon) are relatively inert towards corrosive media. The interaction of powdered "cluspol" materials with hydrochloric and with hydrofluoric acid (diluted with water in a ratio of 1:1) and with bromine at 50 °C for 5 h has been studied[6]. No significant breakdown of the material was noted, but the colour of the powder changed from black to dark grey, and a small amount of metal was transferred to the solution. Thus, at

an iron concentration of 7.39 wt.%, 14% of the iron originally present was extracted into the solution.

The low-angle X-ray diffraction curves for these samples (Fig.8) show that acid treatment of the HPPE + Fe material tends to wash out the clusters with $d \geq 60$ Å. In the NMR spectra of the treated smaples a narrow component appeared with the broad component, though it had been previously established that this NMR component does not occur in polyethylene containing more than 3 wt.% of iron. These results suggest that the localisation sites of the larger ($d > 60$ Å) clusters are in the outer, mainly amorphous regions of the polymer particles. The remaining clusters (15–20 Å in diameter) are formed in the holes of the structure and are strongly held there. In polyethylene the localisation sites of the 15–20 Å clusters are probably crystal defects (in the crystalline regions) and holes (in the amorphous phase).

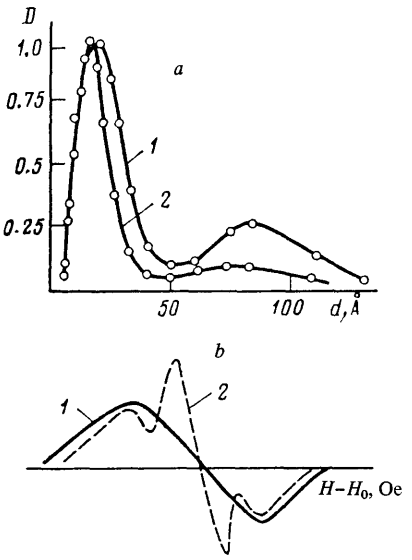


Figure 8. Changes in particle size distribution from low-angle X-ray diffraction results (*a*) and from the shift in the NMR spectra (*b*) produced by acid treatment of "cluspol" samples: *1*) initial sample, *2*) sample treated with HCl.

Thus we have developed a method of preparing "cluspol" materials containing metallic clusters with a narrow size distribution in polymeric matrices of the polyethylene and Teflon type. We have shown that the method is applicable to a wide range of metals and to different matrices. From a combination of physicochemical and structural studies we conclude that the metal clusters are located in natural holes of the polymer matrix, where they interact strongly with the matrix. The properties of the material and its physicochemical characteristics (magnetic, electrical, etc.) do not point to the presence of a metallic phase. The strong cluster–polymer interaction produces quasi-crystalline properties in the polymer matrix. Thus the materials of the "cluspol" type can be treated as single-phased metal–polymers in certain ranges of metal concentration.

Studies of the properties of these materials have only recently started: two types of characteristic (electrophysical, and magnetic properties) have been examined.

4. Electrophysical Properties of "Cluspol" Materials

The polymer matrices used for the preparation of "cluspol" materials are typical dielectrics. The addition of metallic particles to dielectrics in order to obtain electrically conducting polymer composites has long been a standard procedure in industry (in particular, electronics and radio), to give electrically conducting coatings, adhesives, etc.[58,59] The metal content of these composites is usually several tens of per cent by weight, and the particle size of the metal varies from a fraction of a micrometer to tens of micrometers.

Table 3. Electrical resistivity of "cluspol" composites.

No.	Sample	[Fe], wt.%	*R*, Ohm m
1	Teflon-40	20	10^{13}–10^{14}
2	Teflon-40	30	14
3	HPPE	20	$2.4 \cdot 10^2$

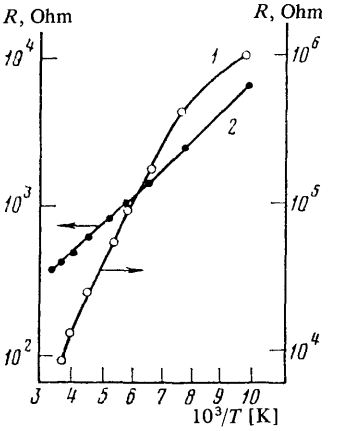


Figure 9. Resistance of "cluspol" samples against reciprocal temperature: *1*) PTFE + 30 Fe, *2*) HPPE + 20% Fe.

In "cluspol" materials the metallic clusters are accommodated in natural holes of the polymer matrix, at average distances from each other of 90–220 Å (depending on the metal concentration). This configuration of the clusters excludes the possibility of direct contact between metal particles and the formation of electrically conducting channels. Our electrophysical measurements on samples of "cluspol" materials (see Table 3) show that the addition of iron clusters to the polymer matrix can lower its electrical resistivity from 10^{15}–10^{16} Ohm m (a typical value for polymers such as HPPE and PTFE) to as little as 14 Ohm m (a typical semiconductor value).

These results also show that the resistance is very sensitive to the sample preparation conditions. For example, sample No.2 was prepared by pressing the powder into a cylinder at 120 atm and 280 °C, and used to study the variation of resistance with reciprocal temperature. We note from the results (Fig.9) that the electrical conductance increases with temperature in the experimental temperature range. The

plot is very similar to comparable plots for typical semiconductors.

Thus the electrophysical properties of polymers can be controlled between wide limits by introducing metallic clusters into natural holes of the polymer. However, more detailed and comprehensive studies of these effects are needed.

5. Magnetic Properties of "Cluspol" Materials

The static magnetic properties were measured for concentrations between 0.1 and 30 wt.% of iron at temperatures between 1.6 and 300 K with fields of up to 10 kOe (Fig.10). A characteristic temperature (T_m) corresponding to a maximum in the plot of magnetisation against temperature was observed in all samples cooled from 300 K to 4.2 K in the absence of a magnetic field. This maximum disappears if the sample is cooled in a field[60,61].

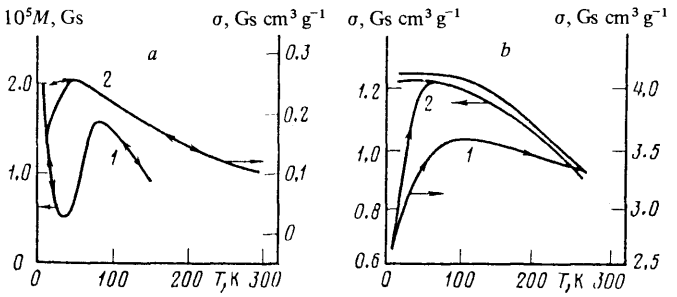


Figure 10. Temperature dependence of the magnetisation of samples containing different amounts of metal: (*a*) *1*) PTFE + 1% Fe, H = 10.2 kOe; *2*) PTFE + 5% Fe, H = 10.2 kOe; (*b*) *1*) PTFE + 30% Fe, H = 1.9 kOe, *2*) HPPE + 30% Fe, H = 1.3 kOe.

The magnetic properties are determined by the ensemble of superparamagnetic particles of the given metal, whose crystal structure differs from that of the massive metal. For the PE + Fe samples we have shown[56] that the change in structure is caused by the influence of the polymeric macromolecules; analogous effects are reported in Ref.62. The change in crystal structure of the particles produces sharp changes in magnetic properties. In iron and cobalt the effective anisotropy constant of the crystal field is increased[61]. Below the temperature T_m, determined by the locking temperature T_{lock}, the magnetic moments of the iron and cobalt particles are "frozen" in the anisotropic crystal field. The presence of T_{lock} makes the magnetic properties of the sample a function of the cooling conditions (as in the case of the spin glasses). In the PE + Cr samples the magnetic moments of the particles remain unfrozen down to 1.6 K (possibly because of their very small size). The iron metal–polymers contain, in addition to particles with $d \geqslant 100$ Å, much smaller particles which remain supermagnetic down to 1.6 K.

Thus our results show that the exchange and other collective interactions between particles of metallic clusters are retained in "cluspol" materials.

IV. POSSIBLE APPLICATIONS OF "CLUSPOL" MATERIALS

At the present stage of development insufficient data are available for the fields of application of the new material to be identified. It appears likely, however, that these materials will be exploited as thermally stable materials, as magnetic materials with properties similar to those of amorphous magnets and spin glasses, and as a new class of semiconducting polymers offering a wide range of parameters.

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The Technology, Structure, and Properties of Organosilicon Dielectrics-polyorganosilasesquioxanes

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The available information about the technology of the preparation of polyorganosilasesquioxanes, their structure, and properties is described systematically, surveyed, and compared with that on inorganic oxide dielectrics. The possibilities and advantages of their application as dielectric materials in semiconductor electronics are examined; analysis of the experimental literature data has led to the conclusion that the method of preparation has a decisive influence on the mechanism of the formation of oligomer molecules their conversion into polymers, and their interaction with various supports.
The bibliography includes 281 references.

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I. INTRODUCTION

The development of the leading branches of the national economy such as power engineering, electronics, computer technology, electrical engineering, radioengineering, instrument making, etc. is linked directly to the accelerated incorporation in industry of new physical principles and expansion of the applications of those already known. This is possible solely on the basis of materials with characteristics conforming to the maximum extent to their functional purpose[1].

One of the most widely used materials in modern electronic engineering is single crystal silicon[2,3], on the basis of which a whole range of semiconductor devices has been created. The importance of silicon as a general purpose semiconducting material will not diminish in the future. Following the expansion of the assortment of special purpose semiconductors such as compounds of the type $A^{III}B^{V}$, $A^{I}B^{V}$, $A_2^{II}B^{IV}$, $A^{II}B^{V}$, $A^{II}B^{VI}$, oxides, chalcogenides, ternary and more complex inorganic compounds[2,3], and organic semiconductors[1,4], silicon will be employed still more vigorously and economically in electronic structures where its useful properties are most fully realised.

II. DIELECTRIC MATERIALS IN ELECTRONIC INSTRUMENT MAKING

The necessity to employ dielectric materials in the manufacture of semiconductor instruments[3,5] and integrated circuits is generally known. In metal–dielectric-semiconductor metallic structures (MDS structures) or, as a special case, metal–oxide–semiconductor structures (MOS structures), the dielectrics are active structural elements. Furthermore, oxide dielectrics are used in the technology of semiconductor instrument making as masks in thermal diffusion or ion beam doping processes[6-8]. Amorphous silicon dioxide, formed either by the thermal oxidation of the surface of a single crystal[9,10] or by the decomposition of organosilicon compounds, for example, pyrolysis, hydrolysis, or treatment in a glow discharge plasma[11-13], is widely used in silicon devices. The influence of the conditions of preparation on the quality of amorphous silicon dioxide films has been examined[14-17] and the dependence of the electrical strengths of the films obtained by different methods (thermal oxidation in dry oxygen, high-frequency and reactive deposition) on the method of preparation has been established[15]. As in prolonged annealing in an atmosphere of nitrogen at temperatures in the range 250–500 °C,[14] an increase of the defectiveness of the film is due to the development of pores all the way through the film and the formation of microcrystallites in the amorphous dielectric. The processes involved in the preparation of silicon and titanium oxides without carbonaceous impurities (the limiting impurities for a dielectric on the surface of silicon in view of the possible carbidisation) by the hydrolysis of the corresponding tetraethoxy-derivatives have been subjected to thermodynamic analysis[16] and the process conditions have been determined.

The influence of the properties of amorphous silicon dioxide on the parameters of silicon MOS structures has been examined in detail in a number of studies[10,18-35]. Analysis of the results[19-21,32,33,35] has led to the concept of the structure of the silicon single crystal–amorphous SiO_2 system illustrated in Fig.1, from which one can see the complex structure of the transition layer incorporating both the material of the single crystal, as a result of the dissolution of oxygen in the surface regions and the formation of additional surface and interphase[35] states of different kinds, and to an even greater extent the material of the amorphous dielectric particularly near the interface. The amorphous SiO_2 on the surface of a silicon single crystal is distinguished by a pronounced layer inhomogeneity and undergoes a series of phase transitions depending on the distance from the interface.

Region I (Fig.1) of amorphous SiO_2 (distance up to 10 Å), incorporated in the transition layer, is characterised by the non-stoichiometry of the oxide[19,21,22,33] and the presence of incomplete hydrated and distorted silicon–oxygen tetrahedra[19]. It is followed by region II (between 10 and 30 Å), consisting of amorphous material with a pseudo-coesite structure, which is due to the operation of compressive forces (the compensating stretching forces act on the silicon single crystal). The relaxation of the internal stresses[22,31] in the $Si–SiO_2$ system, which occurs mainly in this region, leads to local breaks in the continuity of the layer. It is significant[31] that, regardless of the oxidation conditions, the grown oxide may be metastable and the structural mechanical stresses in it do not relax fully. Region III is a zone of the phase transition[20] from the non-equilibrium pseudo-coesite structure to the pseudotridymite structure of the bulk-phase oxide characteristic of amorphous SiO_2 (region IV). This phase transition is characterised by an intensification of the $p_\pi d_\pi$ interaction and therefore extends up to 30 Å.

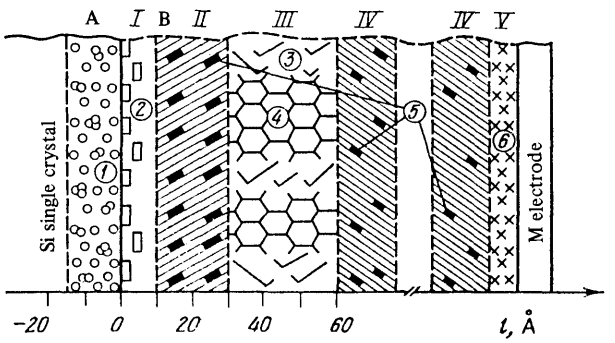


Figure 1. Schematic illustration of the MOS structure on silicon with thermal oxide[19–21,32,33,35]: region A—stretching stresses relaxation zone in a silicon single crystal saturated with interstitial oxygen atoms and clusters (1); region I—transition region corresponding to the non-stoichiometric oxide SiO_x (with $x < 2$) containing inclusions of polycrystalline SiO_2 (2), concentrated predominantly in the immediate vicinity of the interface; region II—existence of the oxide in the short-range and long-range order pseudocoesite modifications with inclusions of nuclear crystals of the oxide (5); region B = region I + region II—compressive stresses relaxation zone in the amorphous oxide; region III—region of the pseudocoesite—pseudotridymite phase transition with dislocation boundaries (3) and hexagonal channels (4); region IV—characteristic region of the bulk of the oxide existing in the short-range and long-range order pseudotridymite modifications with inclusion of 10–50 Å nuclear crystallites of the oxide (5); region V—region of the oxide near the electrode with an incorporated limited space charge and atoms of the electrode metal (6) (the monomolecular and multimolecular layers of the metal oxide exist on the surface of the sputtered metallic polycrystalline electrode at the metal–amorphous SiO_2 interface).

The concept of the fragmented spatial atomic network in the bulk of amorphous silicon dioxide, formed by a mosaic of self-limited ordered clusters–rings formed by 4, 6, and 8 silicon–oxygen tetrahedra, is being developed[20]. The internal boundaries of regions II and IV constitute a system of hexagonal channels and the coesite–tridymite phase transformation region III leads to the formation of extensive defects–assemblies of dislocations. It is difficult to agree with one of the conclusions of the authors of the above studies[20], namely that the multilayer structure of the thermal SiO_2 film is the main cause of the high degree of perfection of the SiO_2/Si system. This conclusion must be compared with the results of other investigations of the structure of the layer of amorphous SiO_2 on single crystal silicon[19,21] from which follows the necessity to take into account the heterogeneity of the material of the oxide film within the layer, in particular, the formation of nuclear crystallites within the bulk of the film with dimensions amounting to tens of angstroms and of polycrystalline inclusions and local discontinuities near the interface[21].

Thus there is a metastable compensation of various defects in the $SiO_2–Si$ system, which is the reason for the marked dependence of the quality and characteristics of the resulting electronic structures[29,34] on the conditions of their formation. In MOS structures it is necessary to take into account also the characteristics of region V—the zone of the dielectric near the electrode, the properties of the dielectric–metal contacts, and the nature of the metal[26]. The phenomena involving the heterogeneity of amorphous silicon dioxide examined above determine the charge instabilities and fluctuations[10,25,27] and their dependence on external factors: the influence of optical radiation[28], γ-radiation[23,24], the presence of impurities[24], and ion transport[30]. In connection with the foregoing, the claim[18] that the properties of vitreous substances are most clearly related to their structure in terms of "average order" is valid.

The influence of the transition layer between the semiconductor single crystal and the amorphous oxide dielectric, which to a large extent determined the concentration of the interphase and surface states of the single crystal, is manifested more distinctly when one used, instead of silicon dioxide, other oxides in the MOS structures, for example, titanium dioxide. In contrast to silicon dioxide, the titanium dioxide layer cannot be grown thermally on the surface of a silicon single crystal and the usual method of its deposition consists in decomposing organotitanium compounds[8,16,36]. The temperature dependence of the degree of crystallinity of titanium dioxide films on single crystal silicon under sputtering and annealing conditions has been published[36] and a schematic description of the structure of the system has been presented: a TiO_2 film on single crystal silicon at different deposition and annealing temperatures. It was observed that, at any TiO_2 deposition temperature, a multicomponent heterogeneous system is formed in which there is a more or less extensive transition layer, the degree of crystallinity of the film increasing sharply with increase of temperature. At a deposition temperature in excess of 550 °C, three phases coexist in the material of the oxide: amorphous phase, anatase, and rutile, while at the optimum decomposition temperature for organotitanium compounds (725–925 °C [16]), almost completely crystalline titanium dioxide (rutile with anatase inclusions) is produced. Furthermore, under all deposition conditions, a more or less extensive polycrystalline transition layer is present in the single crystal–oxide system.

The increase of the instability of the amorphous state in connection with the formation of polycrystalline structures is possible in many technological processes for the preparation of thin oxide films. For example, in the preparation of two- and multi-layer oxide films of the $SiO_2–Al_2O_3$ type[37], there is a possibility of the formation of polycrystalline silicates, while

the interaction of complex oxides in the formation of protective oxide films obtained by anodising the surfaces of semiconductor crystals of the $A^{III}B^{V}$ and $A^{II}B^{VI}$ type can also lead to the formation of polycrystalline compounds. The most general process for these semiconductors involving the deposition of dielectric coatings is therefore the decomposition of organoelemental, usually organosilicon, compounds or silicon halides and hydrides. Depending on the process conditions and the composition of the gaseous or vapour phase, SiO_2 or silicon oxide nitride (SiON) is formed on the surface of the semiconductor single crystal. A transition layer containing the products of the chemical reactions of the material of the film and the single crystal is formed at the interface. The formation of an interface between GaAs and InP semiconductor single crystals and the amorphous dielectrics SiO_2 and SiON deposited chemically on them from the vapour phase has been described[38]. The properties of the interface and the structure of the insulating layers depend greatly on the process temperature and the chemical nature of the semiconductor single crystal. The general inhomogeneity of the dielectric coating has been noted.

The use of organisolicon polymers in electronic engineering holds out most promise and this is in fact the subject of the present review. On must note that such prospects are based on serious experience gained in the industrial manufacture and applications of organosilicon resins and varnishes[42–46] in electronics and semiconductor instrument making.

III. THE SYNTHESIS AND TECHNOLOGY OF THE PREPARATION OF OLIGO-ORGANOSILASESQUIOXANES

The founder of the chemistry and technology of organosilicon compounds is academician K.A.Andrianov, who began his researches in this field in the 1930's and has consistently developed various fundamental and applied fields of organosilicon chemistry, in particular the chemistry and technology of organosilicon polymers.

This review is devoted to the technology, structure, and properties of oligo- and poly-organosilasesquioxanes (OOSSO and POSSO), i.e. organosilicon compounds with a functionality up to three and above. Subsequently the term "functionality (F)" will be understood as the average functionality of the initial mixture of organochlorosilanes (OCS), corresponding to the number of chlorine atoms bound to the silicon atom and involved in the hydrolytic condensation reaction. Compounds with $F = 2.0$ and, in particular, siloxane rubbers have been described in detail in a monograph by Voronkov and co-workers, which lists 5000 references[50], while the industrial technology and certain applications of polyorganosiloxanes have been described in monographs[51,52] and in another publication[53].

The expression "functionality of the oligomer (polymer)" implies that the compound has been obtained by the hydrolysis of a mixture of OCS having the same functionality.

We shall consider mainly studies which have not been covered by earlier surveys[50–52].

1. Preparation of Oligo-organosilasesquioxanes

The preparation of soluble and fusible OOSSO leads to new possibilities in the technology of electronic instrument making. OOSSO hardened directly on a support have come to be used in specific semiconductor instruments and integrated circuits, where they serve as materials of passivating films, active dielectric layers, protective coatings[54–56], and thermal diffusion masks[57] instead of silicon dioxide, obtained traditionally by oxidising the surface of single crystal silicon or by decomposing organosilanes.

In the periodic synthesis of OOSSO [58,59] there is a great probability of the formation of an infusible and insoluble skeletal polymer—gel, while in the hydrolysis of OCS with large substituents there is less likelihood of such a process[60].

The preparation of general purpose dielectrics requires oligomers without a microgel and with a low carbon content (with small substituents), which are synthesised by the appropriate organisation of the technological process.

The residence time of the OCS in the periodic type of reactor is determined by the sum of the time taken to prepare the reactant charge, the reaction time, and the time taken to remove the product. The residence times in the reactor for the first and last portions of the OCS therefore differ greatly, which leads to a considerable scatter of the molecular weights of the resulting OOSSO and the formation of large amounts of gel. The contact time between OCS and the reaction mass in a continuous operation vat reactor with stirring can also differ greatly for the first portions of the reactant according to Levenspiel[61] and Reikhsfel'd et al.[62] Only two-thirds of the OCS introduced is passed straight through the reactor and its contact time is equal to the time taken to traverse the volume of the reactor; 1–3% of the reactant remains in the reactor in constant circulation. With this organisation of the technological process, it is difficult to avoid gel formation and a considerable scatter of the molecular weights of the resulting oligomer. It has been shown[57] that the use of such an oligomer as the electronic resistor for thermal diffusion masks on a semiconductor support does not lead to optimum results.

Other ways of obtaining oligomers without a microgel and with a narrow molecular weight distribution (MWD) in a periodic reactor are possible. Higher alkyltrichlorosilanes with a number of carbon atoms n_C in the substituent between 6 and 10 have been hydrolysed in concentrated hydrochloric acid at the normal pressure[63]. This results in the formation of comparatively low-molecular-weight substances with a high content of hydroxy-groups and having the general formula $[RSiO(OH)]_n$, where R = C_6H_{13}, C_7H_{15}, C_8H_{17}, or C_9H_{19} and $n = 6$ or 8; they are readily soluble in benzene, toluene, and ether and on heating are converted into liquid alkylsilasesquioxanes having the general formula $[RSiO_{1.5}]_{6;8}$. Their hydrolysis in the absence of a solvent results in the formation of stable emulsions in this instance. It has been suggested that the hydrolysis of higher OCS be carried out under a pressure of 15–80 atm with 0.165–0.465 mole of water per Si–Cl bond[64]. The hydrolytic reaction proceeds via an intermediate[65]. A method has been proposed[66] for the preparation of the oligomer by the hydrolysis of tetraethoxysilane in ethanol. All these methods, which are of undoubted preparative interest, suffer from many disadvantages from the standpoint of the preparation of high-quality dielectric films and coatings for semiconducting materials because the oligomers obtained have a high ineradicable impurity content.

One of the few instances where the periodic organisation of the technological process does not entail a reduction of quality and involves merely a decrease of the yield of the desired product is the synthesis of octaorganocyclo-octasilasesquioxanes[67], for example, octavinylcyclo-octasilasesquioxane[68] or ethylvinylcyclooctasilasesquioxane[69]. A characteristic feature of these compounds are that they can be isolated from the mixture of reaction products by sublimation in the form of pure substances, undergoing a comparatively far-reaching purification under these conditions.

2. The Preparation of OOSSO with Small Aliphatic and Aromatic Substituents

A general purpose dielectric for electronic engineering must meet fairly rigorous requirements—all its dielectric characteristics (ε, $\tan\delta$, ρ_V, E_{br}, the space charge Q_V, and the surface charge Q_S) must be at least not inferior to those of the pyrolytic silicon dioxide and at the same time must ensure either the possibility of the realisation of new physical principles in electronic instrument making or must have sufficient technological advantages which would justify the expenditure on its development and employment. With the periodic organisation of the process or in a discontinuous action vat reactor, it is impossible to obtain products satisfying the above requirements.

One of the most important methods of terminating the growing chain in three-dimensional polycondensation involves the cyclisation reaction[70]. The cyclisation processes in the hydrolytic condensation of OCS are most influenced by the hydrolysis conditions.

On the basis of the foregoing considerations and a number of investigations[60,70-80], one can formulate the principal requirements to be met by the continuous process involving the hydrolytic condensation and cocondensation of OCS, particularly when the functionality of the mixtures to be hydrolysed is $F \geq 3.0$: (1) no mixing of the reaction products with the initial OCS; (2) a minimal residence time of the reaction products in an acid medium; (3) effective removal of heat from the entire volume of the reactant; (4) the universality of the hydrolytic condensation of various OCS and their mixtures with $4.0 > F \geq 2.0$; (5) simple scaling.

For the given conditions, the above requirements are satisfied to the greatest extent by the technological formulation of the processes put forward and justified by Andrianov et al.[70]

In view of the high lability and instability of silanols (the intermediates in the hydrolysis of OCS), the study of the condensation process is difficult. However, this process can be described qualitatively from the standpoint of the kinetics of homogeneous chemical reactions[81,82].

Since the hydrochloric acid formed in hydrolytic condensation catalyses further condensation reactions of the Si–OH groups, an important task in the organisation of the continuous operation process is the regulation of its overall rate. This is achieved by familiar procedures[83]: by introducing an acceptor into the reaction mixture which binds chemically the hydrogen chloride, by analogy with the continuous procedure for the synthesis of tetrabutoxytitanium[36,83]; with the aid of high dilution (with a high yield of cyclic products)[84]; using monomers with large organic substituents at the silicon atom[63,85]; by the preliminary partial alkoxylation (acylation) of the organotrichlorosilanes, as in the industrial preparation of the KO-928 varnish.

In the course of the subsequent hydrolytic condensation, the partly esterified products[80] behave like bifunctional OCS, since the rate of hydrolysis of the Si–Cl bond is much higher than that of the Si–OR or Si–O–COR bond[86].

The hydrolytic condensation of OCS or OCS systems with a high functionality and a small substituent at the silicon atom, in particular the methyl substituent, is accompanied by the formation of methylsilanols, which are extremely labile and sensitive to changes in the pH of the medium[87].

A straight glass condenser with an internal diameter of 20 mm and 700 mm high can serve as a laboratory model of the reactor for the continuous hydrolysis of lower OCS.[70] Under industrial conditions, for example, in the manufacture of the KO-812 varnish, a tubular reactor with the same diameter and height of the tube is used, which is necessary to maintain the hydrodynamic and heat and mass exchange conditions. Laboratory apparatus for the preparation of a solution of oligo-organosilasesquioxane without a microgel is illustrated in Fig. 2. Solutions of oligomers with functionalities in the range $2.0 \leq F < 4.0$ can be prepared on such apparatus[70], which has been demonstrated in relation to a series of industrial recipes for organosilicon resins and varnishes, for example K-5, K-9, K-81, and KM-9. In the lower part of the reactor there is an atomiser through which a solution of chlorosilane is introduced into the water entering the reactor. The volume flow rate of the components is 2.8 ml s^{-1}, which corresponds to an average flow rate of the reaction mixture in the tube of 30 mm s^{-1}. For a specified kinematic viscosity ν, these conditions determine a Reynolds number $Re \cong 300$. For these values of Re and in the absence of perturbations at the inlet, the flow in circular tubes is laminar, which makes it possible to neglect diffusion as a slower concentration equalising process. For the same reason, the temperature and the flow rate are constant throughout the cross-section.

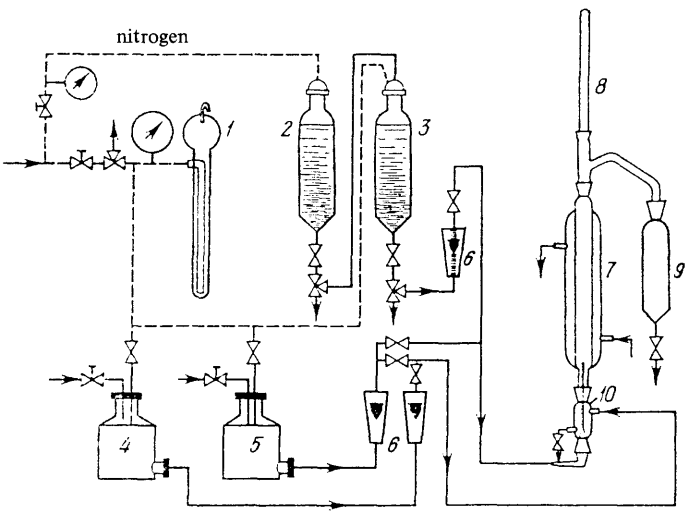


Figure 2. Schematic illustration of the laboratory apparatus for the continuous hydrolysis of organochlorosilanes[73,88]: 1) manostat; 2) reservoir for the preparation of OCS solutions; 3) OCS supply reservoir; 4) water supply reservoir; 5) acetone supply reservoir; 6) flow meters; 7) reactor; 8) thermometer; 9) receiver; 10) partitioning device.

Near the inlet for the OCS solution into the reactor, vigorous turbulent mixing takes place due to the chemical hydrolysis of the OCS, with local evolution of much heat and hydrogen chloride, and also a velocity gradient. The eddy relaxation time τ_V is equal to the ratio of the cross-section of the characteristic volume ($S_p \cong 1$ cm^2) to the viscosity ($\nu \cong 0.01$ cm^2 s^{-1}) and amounts to $\tau_V \cong 100$ s. Comparison of the reaction time $t_r \cong 20$ s and τ_V shows that turbulent mixing of the substance within the limits of the isolated volume takes place throughout the reaction time.

Thus the reaction zone is divided into two sections—the vicinity of the site of injection of the reactants and the rest of the reactor; the hydrolytic condensation reaction of trichloromethylsilane (TCMS) can be regarded as occurring

in two stages: the three-step irreversible hydrolysis of TCMS and the condensation of methylsilanetriol. Since the reaction in the first step proceeds during a very short charactertisic time ($\tau_2 \ll 10^{-2}$ s), one may claim that the entire TCMS hydrolyses during a period shorter than 1 s, which corresponds to the region of the reactor near the nozzle of the atomiser (size ~35 mm), from which the solution of the monomeric methylsilanetriol at a concentration equal to that of the initial TCMS (c_0) enters the reactor.

Methylsilanetriol dimers are formed in the reactor:

$$2H_3CSi(OH)_3 \xrightarrow{k_1} H_3CSi(OH)_2-O-Si(OH)_2CH_3 \quad , \qquad (1)$$

and methylsilanetriol adds to the oligomer:

$$H_3CSi(OH)_2-O-[-Si(CH_3)(OH)-O-]_n-Si(OH)_2CH_3 + \\ + H_3CSi(OH)_3 \xrightarrow{k} H_3CSi(OH)_2-O-[-Si(CH_3)(OH)-O-]_{n+1}-Si(OH)_2CH_3 . \qquad (2)$$

The methylsilanetriol condensation processes are bimolecular, so that the rate of formation of dimers via reaction (1) is defined as $k_1c_1^2$ and the rate of addition of methylsilanetriol via reaction (2) to the oligomer is kc_1c (here c_1 and c are the current concentrations of methylsilanetriol and the oligomer respectively).

The onset of the condensation of silanetriol via reactions (1) and (2) is characterised by the conditions $c \to 0$ and $c_1 \cong c_0$, so that $kc_1c \ll k_1c_1^2$. Hence it follows that the rate of addition must become appreciable only in the final stages of the condensation, but in this case it is also low because by that time virtually no unreacted methylsilanetriol remains in the reaction medium.

In contrast to the studies by Roberts[57] and Pruvost et al.[72], in the investigations of Andrianov and co-workers[70,71,82] reaction conditions ensuring the complete suppression of the gel formation process were rigorously maintained. The formation of the microgel begins when the average length of the siloxane chain ($\bar{L}$) corresponds to ten or more monomer units [$n \geq 8$ in the equation of reaction (2)]. The increase of $\bar{L}$ for all the molecules, for example by a factor of two (due to the condensation of pairs of molecules), is associated with a decrease by a factor of two of the concentration c. Consequently synthesis without the formation of a gel requires that $c \cong 0.1c_1$ during the time $t_r \cong 20$ s. The rate constant $k_1 \cong 1 \times 10^4$ and $K = 1 \times 10^3$ ml mol^{-1} s^{-1}, which depend both on the composition of the reaction medium (the nature and proportions of the solvents, the initial concentration of TCMS, etc.) and on the reaction conditions (temperature, contact time, etc.), satisfy such conditions.

Similar requirements to be met by the process conditions hold also for other OCS with a high functionality—trichlorovinylsilane and trichlorophenylsilane, as well as the products of their cohydrolysis with one another or with TCMS, dichlorodimethylsilane, silicon tetrachloride, and polysilicic acids[71,78,89–112]. The influence of the conditions of the synthesis on the relative contributions of the homofunctional and heterofunctional pathways in the hydrolytic condensation and hence on the composition of the reaction products has been noted in studies of hydrolysis of TCMS [70,71,77,83,113,114] and of the hydrolysis of trichlorovinyl- and trichlorophenylsilanes, the cohydrolysis of various OCS having small substituents, and the cohydrolysis of OCS with silicon tetrachloride and polysilicic acids[78,79,83,87–90,98–106,112]. The generality of the competitive mechanism of the linear chain propagation and cyclic compound formation reactions can be demonstrated in relation to the trimethylsilylation of the inorganic compound $Ag_{10}Si_4O_{13}$, which leads to the cyclisation of the linear chain anion $Si_4O_{13}^{10-}$,[115] by analogy with the hydrolysis of trichlorophenylsilane[99], which leads to the formation of the xonotlitic ribbon [or double chain (Ed. of Translation)] oligomers.

As was to be expected from Eqns.(1) and (2), on decrease of the water:TCMS ratio, the content of the oligomer in the organic phase increases and the losses of the water-soluble products in the aqueous phase diminish. However, when the reaction is carried out when there is a deficiency of water, the scatter of the molecular weights of the products may increase. The methods for the investigation of the hydrodynamic process parameters are applicable to the analysis of the products of the hydrolytic condensation of OCS.[100,101,116]

The kinetics of the hydrolytic condensation of OCS as a whole have been considered[77,81,82,113]; in order to obtain quantitative information about the kinetics of reaction (2), it is apparently useful to employ the kinetic method for the calculation of the MWD of the chains between the branching nodes in non-equilibrium polycondensation reactions[117].

In order to obtain materials with the required characteristics, it is important to know the influence of the conditions and various factors on the formation and structure of the oligomers directly in the technological process[88,90], since the structure ultimately determines, for example, the defectiveness and the film-forming properties of the coatings. It has been stated[79,98,102] that, in the cohydrolysis of trichlorophenyl- and trichlorovinyl-silanes, the resulting mixture does not contain the products of the separate hydrolysis reactions and the fractions of the oligomers and polymers retain the initial ratio of the phenyl and vinyl substituents (3:1).[79]

The hydrolytic condensation of TCMS yields a product which is a complex mixture of polycyclic derivatives with various structures. The synthesis of oligomethylsilasesquioxane in a total displacement flow-type reactor with the parallel injection of reactants in a complex acetone–toluene solvent[118] using the thermostatic attachment has been described[88]. The influence of the synthesis temperature on the physicochemical and electrophysical characteristics of the resulting materials has been investigated. The experimental data indicate an increase of the degree of reaction with increase of temperature (Fig.3).

3. Optimisation of the Continuous Hydrolytic OCS Condensation Process

The hydrolytic reactions of OCS permit the variation of the ratio of the solvents and water within fairly wide limits[70,72,77,78,90,104–106,113]. A significant alteration of the process conditions can change the composition (see, for example, Andrianov et al.[114]) or the structure[89,105] of the hydrolytic condensation products.

The necessity to obtain materials with specified properties brought to the fore the problem of optimisation, whose solution makes it possible to automate the continuous hydrolytic OCS condensation process.

For example OCS systems with $F \geq 3.0$ and a small organic substituent are extremely unstable and tend to form gels. The ratio and the order of introduction of the reaction components, for example, TCMS, acetone, toluene, and water, are important in the hydrolytic condensation of such systems[71,77,83,88].

A definite component ratio for which the process could be carried out without gel formation when acetone is introduced simultaneously with the solution of TCMS in toluene has been found experimentally[70,72]. This ratio has been adopted[118] as a basis in devising an optimisation design. The aim of the optimisation was to reduce the consumption of solvents whilst ensuring the formation of a product free from a gel. In order to minimise the consumption of solvents, a consecutive simplex optimisation method was used, because it is

effective in the solution of problems with several responses and limitations.

Optimisation yielded a point with a minimum consumption of solvents (2.81 litres of solvents per litre of TCMS, which is smaller by a factor of 2.6 compared with the periodic process—by a factor of 2.3 with respect to acetone and by a factor of 3.8 with respect to toluene[118]). Tests[71,88] for the stability of a technological regime without gel formation made it possible to recommend the following amounts of the solvent components per litre of TCMS in the process to be carried out under practical conditions: 2.3 litres of acetone, 0.7 litre of toluene, and 2.3 litres of water (temperature 40° ± 5 °C).

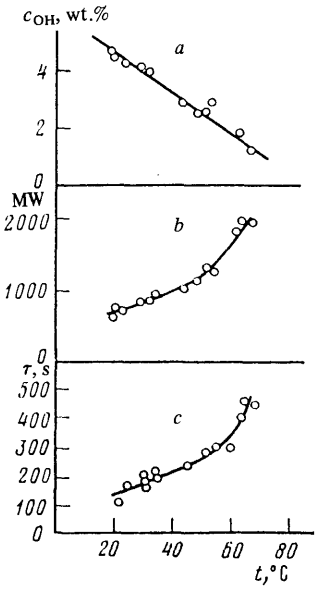


Figure 3. Dependence of the properties of oligomers on the temperature of the synthesis t:[88] *a*) content of hydroxy-groups c_{OH}; *b*) average molecular weight $\overline{MW}$; *c*) gel formation time τ at 200 °C.

The concentration of the required products in the extract and the refined material (in the case of the hydrolytic OCS condensation in the organic and aqueous stages respectively) and the degree of extraction of the reaction products are extremely important technological characteristics of the combined processes involving both chemical interaction and extraction.

The characteristics of the influence of the parameters of the continuous synthesis of OOSSO in a flow type reactor on the concentration of oligomers in the organic and aqueous phases, the content of the hydroxy-groups in the oligomer, the gel formation time, and other characteristics of the hydrolytic condensation products have been investigated[71,77,83,88,113,118].

In conformity with the adopted aim, the concentration of the oligomer in the organic phase, determined from the content of the dry residue, was adopted as the response function and the process temperature, the specific consumptions of acetone, toluene, and water, and the overall volume rate of injection of the components into the reactor were adopted as the factors to be investigated[88,118]. The regression and variance analyses of the resulting equation and its coefficients demonstrated the significance of all the factors investigated except the rate of injection of the reactants (within the limits investigated). The specific consumption of acetone has the greatest influence on the content of oligomers in the organic phase[71,118]; as it increases, the concentration of oligomers falls. The increase of the specific consumptions of acetone and water[71,77,113] leads to a proportional diminution, and an increase of the synthesis temperature[88,118], to an increase of the concentration of the oligomers in the organic phase in the range 19–24%. The concentration of oligomers in the organic phase, calculated from the regression equation for the process carried out under the conditions of the minimum consumption of the solvents, agrees with the experimental value within the limits of the error.

The degree of extraction of the reaction products determines to a large extent whether or not the process is economical. An increase of the synthesis temperature entails a corresponding increase of the yield of the polycyclic products sparingly soluble in the aqueous phase[49,92,114] and hence a diminution of their losses. An increase of the consumption of acetone leads to an increase of the solubility of OOSSO in the aqueous acetone phase and to an increase of the losses. An increase of the consumption of water (a decrease of the concentration of HCl) produces a decrease of the rate of condensation and an increase of the fraction of primary hydrolysis products (organosilanetriols), which are readily soluble in water[49,113] and are carried away with the latter. The complex dependence of the degree of extraction of the products on the consumption of toluene is explained by the fact that the extraction of oligomers from the reaction mixture consists mainly in the extraction from the water–acetone fraction into the toluene–acetone fraction. The initial increase of the degree of extraction with increasing consumption of toluene is therefore associated with the decrease of the solubility of the oligomers in the water–acetone fraction depleted in acetone. A further increase of the consumption of toluene, in which the solubility of the oligomers is low[49], leads to a decrease of the solubility of the oligomers in the organic phase and an increase of the losses of the required product owing to its transfer to the aqueous phase.

The method for the optimisation of the technological process involving the hydrolysis of TCMS can be applied in the study of the hydrolytic condensation of other OCS and the cocondensation of their mixture. Continuous hydrolytic condensation processes with the vinyl-, chloromethyl-, and phenyl-substituted trichlorosilanes have been optimised with the aid of the consecutive simplex method[118] and the data obtained by different workers for the hydrolytic condensation of OCS and their mixtures have been compared[49–51,70,71,77,79,83,87,88,90,92,95,104,113,114].

The possibility of continuous processes involving the hydrolytic cocondensation of TCMS with trichlorosilane, silicon tetrachloride, and polysilicic acid has been examined[89,93–95]. It has been established[70], that the formation of fully soluble products is ensured by carrying out the processes in acetone with subsequent extraction of the reaction products.

4. The Shell Model of the Hydrolytic OCS Condensation Process

The hydrolysable systems in a total displacement reactor have been analysed on the basis of the ideas of the kinetics of homogeneous chemical reactions[81,82] in the presence of

acetone, ensuring homogenisation, in the reaction mixture[121]. However, almost all hydrolytic OCS condensation processes realised in industry proceed as a rule under heterogeneous conditions, which requires allowance for diffusion processes in the study of the polycondensation kinetics. As early as 1959, Sokolov was the first to draw attention to this[119] and proposed a model for the hydrolytic condensation of OCS in a heterogeneous system.

In order to attain a free energy minimum, it is believed[120] that the shell of dispersed-phase species can be divided into several layers. The outer hydrophilic layer consists of solvated molecules of oligo-organosiloxanes. The intermediate layer imparts rigidity to the shell of the globule and consists of oligomers with a wide range of molecular weights. This layer grows as a result of the inflow of the OCS hydrolysis products from the inner cavity within the globule. The inner organophilic layer consists of solvated OCS molecules. Hydrolytic processes, which begin within the inner cavity of the globule, are completed in this layer and the condensation processes, completed in the intermediate layer, begin in it.

The probable mechanism of the heterophase hydrolytic polycondensation was examined above. After the formation of the globules, the rate of reaction is determined by the conditions governing the diffusion of the reactants through the interface[120]. As diffusion processes take place, the intraglobular osmotic pressure increases until the rupture of the shell of the globule accompanied by the ejection into the water–acetone matrix of the contents of the inner cavity of the globule and the formation of a new interface. With decreasing concentration of the monomer, the size of the new globule may not then differ appreciably from the initial size, but the rate of reaction within the globules falls. During the passage of the globule through the reactor, the process involving the rupture of its shell may be frequently repeated.

The above model makes it possible to describe the quantitative picture of the process and to explain the difference in the behaviour of the particles of the solid phase of silica gel or hydrated quartz, tending to coalesce[122,123], and the globules described above, whose surface also contains silanol groups, ensuring the possibility of the polycondensation reaction with formation of siloxane linkages. However, the outer hydrophilic surface of the globules constitutes a barrier which prevents the spontaneous coalescence of the particles coming into contact or colliding. The time of contact between the particles, which in the case under consideration is shorter than 25 s while in the studies quoted above[122,123] it amounted to 10–1000 s, has a definite influence on the aggregative stability of the systems. Nevertheless in the case which we have considered there is also a possibility of the coalescence of the globules when certain process parameters are altered (see, for example, Andrianov et al.[89]), which leads to the formation of an insoluble structured polymer and in some cases also to an uncontrollable reaction—the avalanche-like formation of a gel, which completely blocks the reactor.

The hydrolytic condensation process results in the formation of a solution from which the oligomer can be isolated in the solid state. When the process proceeds with formation of multishell globules, the structure of the oligomers as well as the structure of the polymers obtained from them should depend on the process parameters and the oligomer isolation conditions. An X-ray diffraction study of these relations has been carried out.

The results obtained, presented in Fig. 4*a*, demonstrate the influence of the temperature and the composition of the reaction mass on the changes in the supermolecular structures of the oligomers formed. The degree of crystallinity of all the oligomers is slight (it does not exceed 5%). This precludes a quantitative interpretation of the results—only a qualitative treatment is possible. On the basis of the model of the particle and the process mechanism, the insignificant degree of crystallinity of the oligomethylsilasesquioxanes obtained in acetone can be explained by the decisive influence of the rate of diffusion of the reactants through the outer shell of the globule, which favours the formation of low-molecular-weight crystallisable cyclic oligomers of the type of tetrahydroxytetramethylcyclotetrasiloxane (T_4).

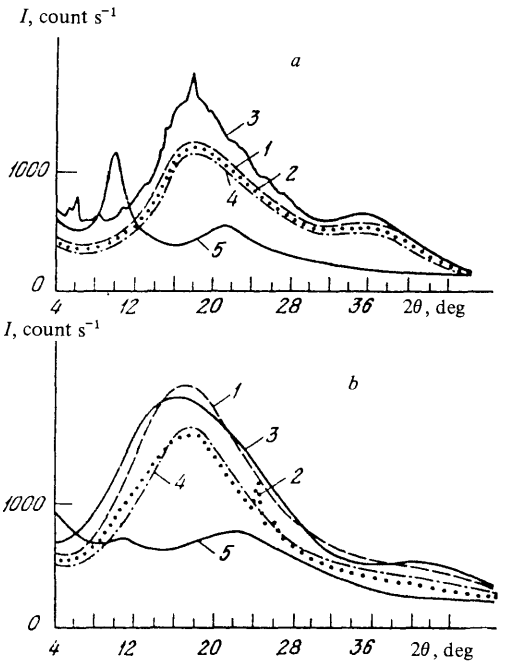


Figure 4. Diffractometer traces for oligo-organosilasesquioxanes (*a*) and polyorganosilasesquioxanes (*b*) (the numbers of the specimens corresponds to those quoted in the Table)[120].

The rate of the subsequent cocondensation of T_4 is reduced as a consequence of the solvation of the hydroxy-groups by acetone. It is significant that the structure of the layer depends on temperature because the constants of the solvation processes and the hydrogen bond formation processes, responsible for the formation of the outer layer, are temperature dependent. When a complex solvent (acetone + toluene) is used, the oligomers formed are amorphous with respect to X-rays.

The data presented in Fig. 4*b* show that the polymers obtained by the condensation of the oligomer containing ~5% of the crystalline phase are fully amorphous, while those obtained by the condensation of the completely amorphous oligomers are apparently crystalline, but the degree of crystallinity does not exceed 5% in this case either.

An additional argument in support of the shell model is the result of the analysis of the width of the first amorphous halo on the diffractometer traces, which is associated with the interchain scattering of X-rays[124,125]. Fig. 4*a* shows the first amorphous halo is extensive (up to $2\theta = 15–18°$), which

indicates an appreciable scatter of the interchain distances, approaching in certain cases 100 Å. Such distances are impossible even for a helical arrangement of the cyclic three-dimensional macromolecules. This indicates the presence of supermolecular formations organised in a more complex manner. The Table lists the half-widths of the amorphous halos calculated from the experimental data (Fig. 4) for the test specimens and, for comparison, the specimen obtained in the presence of a large excess of acetone and water relative to the calculated optimum amount[118]. The Table shows that, while the position of the maximum of the first amorphous halo is relatively constant for all the specimens, its half-width is appreciably altered for the test specimens and is almost an order of magnitude greater than for the control specimen[120].

Dependence of the half-width of the first amorphous halo ($\Delta\theta$) on diffractometer traces for oligomethylsilasesquioxanes on the conditions of synthesis[120].

No. of specimen	T, K	Solvent	$\Delta\theta_1$, deg
1	276	acetone	0.113
2	283	acetone + toluene	0.104
3	280	acetone	0.126
4	278	acetone	0.096
5	313	acetone + toluene*	0.027

*The dilution conditions differ from the optimum conditions calculated by Andrianov et al.[118]

5. Optimisation of the Continuous Process Involving the Synthesis of OOSSO on the Basis of Their Molecular Weight Distribution

In many instances, for example, during the preparation of blended composites, in which it is necessary to ensure an effective distribution of the binder on the filler surface, a wide molecular weight distribution (MWD) is a positive characteristic of the oligomer obtained. Low-molecular-weight reactive cyclic compounds of the type of T_4 or the dimer hexaorganotetrahydroxybicyclotetrasiloxane (T_6) can ensure an even more complete adaptation of the binder as a result of the building up of the oligomeric molecules via a mechanism similar to that of the reactions of siloxanediols with diorganodichlorosilanes[126] or of organocyclosiloxanes with organosilicon diols[127].

However, the attempts to obtain thin dielectric layers and films of polyorganosilasesquioxanes (POSSO) by the polycondensation of the corresponding oligomers lead to negative results in the case of materials with a wide MWD, namely numerous cavities and cracks appear in the film[128], in contrast to the coating obtained on the basis of an oligomer with a narrow MWD.[120]

In order to obtain defect-free structures, one can use one of three methods: the deposition of the polymer or polymerisation on the surface to be protected[11,129–132]; gas and liquid transport chemical reactions and molecular growth ensuring the formation of extremely perfect amorphous oxide films[133–139] (these methods are relatively unsuitable for the formation of polymeric coatings); finally, the preparation of oligomers with a very narrow molecular weight distribution[75, 140] followed by their hardening on the support[109–111].

It follows from the studies devoted to periodic and continuous hydrolytic OCS condensation processes, which dealt with the reaction kinetics[75,81–83,87,88,92–95,104,113,114,141,142] and the MWD of the products formed[49,50,71,75,78,79,88,104,106,120,140], that the formation of products with a narrow MWD can be achieved by altering the conditions in the second stage of the reaction to ensure the predominance of the cyclisation reactions by optimising the process with respect to the MWD of cyclolinear products. The oligomeric intermediates obtained have specific applications depending on the technology of their subsequent converison into the polymer[108–111,140]. The possibility of using cyclic products[71] virtually free of hydroxy-groups as film-forming materials has been demonstrated in studies on the volatility of octaorganocyclo-octasilasesquioxanes (T_8) [69,143] and their polycondensation under the influence of radiation[57,111,140] or catalysts[144–148]. However, despite the comparatively satisfactory characteristics of the films and coatings formed, organocyclosiloxanes with $F \geq 3.0$, in contrast to cyclic compounds with $F = 2.0$,[50] have nowadays found only limited applications[58] in view of the complexity of the technological formulation of the deposition and polycondensation processes, although in the future one may expect their extensive employment in electronics and instrument making as development of apparatus becomes cheaper.

The method of preparation of polymeric dielectric layers from soluble cyclolinear OOSSO, containing 2–4 mole % of hydroxy-groups and with a molecular weight scatter less than 25% is significantly simpler[89,140]. It involves the deposition of solutions of the oligomers on a support by dipping, pouring, pulverisation, or centrifugation with subsequent drying and polymerisation of the material of the film by any of the known methods[52,120,140].

The polymerisation of such oligomers involves preferentially the functional groups and leads to highly cross-linked POSSO [89,140] (as in the study of Katz and Zewi[149]) to which one can apply the statistical model of the structure of a network polymer developed by Topolkaraev et al.[150] for the description of the interrelation between the chemical structure of the initial monomers or oligomers, the kinetics of the condensation reaction, and the technology of the preparation of the network monomer.

In order to obtain oligomers with such characteristics, Kamaritskii[71] used a procedure for the optimisation of the hydrolytic condensation of OCS and in particular TCMS on the basis of the MWD parameters, used as the response, analogously to the procedure described earlier. It has been shown[140] that, when the process is carried out in the vicinity of the new optimum and with a rigorous temperature control in a total displacement flow reactor, it is possible to obtain OMSSO with an average molecular weight $\bar{M} \cong 700$ (with a scatter $\Delta M/\bar{M} \leq 25\%$) and with a hydroxy-group content $c_{OH} = 2$–4 mole %. The products obtained[140] can be described by the revised molecular formula $[H_3CSiO_{1.5}]_{8\pm1.5} \cdot [H_3CSiO(OH)_{1.5\pm0.5}$. The processes involving the subsequent conversion of the OMSSO into the polymer depend decisively on $\Delta M/\bar{M}$ and c_{OH}. The above optimisation has been refined[75] on the basis of the consumption of the raw material components and their ratio taking into account the kinetics of the hydrolytic condensation reaction and, in another study[88], also on the basis of the temperature regime in the process.

6. The Synthesis of Higher-Purity OOSSO; The Possibilities of the Secondary Purification of Oligomers

The dielectrics used in electronic instrument making must meet high requirements as regards homogeneity and purity[151, 152]. The task of improving the materials involves the

improvement of these characteristics or the reduction of the harmful influence of the inhomogeneities or impurities. An example of the reduction of the breakdown characteristics and of the deepening of the breakdown channel, caused by various inhomogeneities in the materials of the dielectrics, has been presented[153].

Polyorganosilasesquioxanes are compounds which are related, on the one hand, to silicates with large cations, forming ribbon structures of the montmorillonite, xonotlite, and kaolinite type[99] (in this sense they fit within the framework of Belov's general classification of silicates[154,155]), and, on the other hand, to silicon dioxide. The properties of silicates and silicon dioxide have so far been investigated in greater detail than those of POSSO, so that the influence of impurities in POSSO can be estimated from their effect on the properties of silicate-based materials which have been studied in detail.

In the industrial manufacture of the KO-812 varnish as well as other organosilicon varnishes[51] and also in the usual laboratory practice, the stabilisation of oligomers in solution is achieved by washing the hydrolytic reaction mixture with a concentrated solution of a salt followed by treatment with KIL clay. The most frequently encountered impurity in POSSO therefore consists of alkali metal ions which are the limiting impurities for silicon and germanium devices and integrated circuits. The Poole–Frenkel' effect has been considered[156] in weak (up to 4×10^5 V cm^{-1}) fields in amorphous silicon dioxide ($E_{br}^{POSSO} \cong 5 \times 10^6$ V cm^{-1}). For films without the limiting impurities, a relation has been obtained between the current density and the applied potential, which has the form usual for the Poole–Frenkel' effect:

$$I = A \cdot \exp\{-(E_{act} - \beta F)^{1/2}/kT\},$$

where the activation energy $E_{act} = 0.2$–1.0 eV, $T = 295$–362 K, and the current density in the oligomers obtained directly by the reaction becomes proportional to n_{Na^+} when the content of sodium ions is only $n_{Na^+} = 10^{17}$–10^{20} cm^{-3}, which is significantly lower than the overall concentration of alkali metal ions (ΣC_M). In oligomers purified to the maximum extent, $n_{Na^+} = 5 \times 10^{13}$–$1 \times 10^{19}$ cm^{-3} and ion transport therefore is unavoidable in MDS structures to which a potential has been applied.

In silica structures there are two types of organisation of the $[SiO_2]_\infty^0$ and $[Si_6O_{17}]^{10-}$ cells—in the form of an infinite three-dimensional network and ribbons of the xonotlite type[157]. The silicates $Ag_{10}[Si_4O_{13}]$ [115] and $[Cu(NH_2CH_2CH_2.NH_2)_2]_4Si_8O_{20}.38H_2O$, incorporating the $Si_8O_{20}^{8-}$ structural element[158] (Fig.5), are similar or analogous to the silicon–oxygen skeleton of the T_8 – $R_8[SiO_{1.5}]_8$ cyclosilasesquioxane (Fig.6).[159] This indicates the similarity of the structural elements of amorphous silica, POSSO, and silicates with large cations and, whereas the possibility of a ribbon–ring transition has been demonstrated[115] for the $[Si_4O_{13}]^{10-}$ anion, in other investigations[49,53] the possibility of the reverse ring–ribbon transition, leading to the formation of a large number of terminal $\equiv$Si–O linkages, at which the alkali metal ions are fixed, has been indicated. The increase of the relative number of non-bridging oxygen atoms[160] and ionogenic terminal groups associated with this factor makes possible both ion and charge transport. These results are important for the estimation of the dependence of the dielectric characteristics of POSSO on the degree of their purification, which follows, for example, from the study of Saratov et al.[161]

The influence of the degree of purification of silicon dioxide on the heats of desorption of the dehydroxylation and de-ethoxylation products has been demonstrated[162,163] and in another investigation[164] the dependence of the activity of silica fillers on the chemical composition has been established, which, as will be shown below, has a significant influence on the character of the reaction at the interface[108].

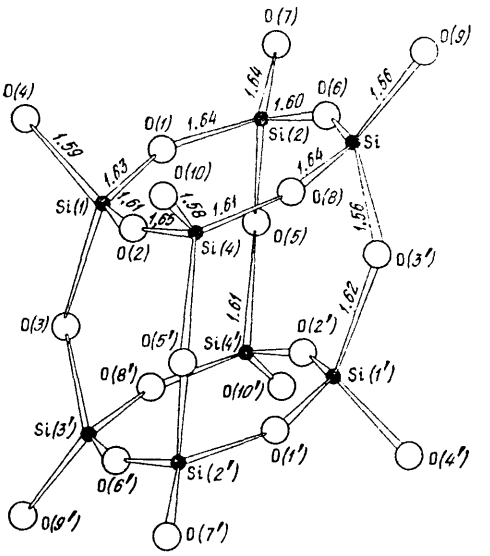


Figure 5. The structure of the skeletal anion $[(SiO_{1.5})_8O_8]^{8-}$.[158]

The sensitivity with respect to active impurities of POSSO with $F \geq 3.0$, having a structure closest to that of SiO_2, and skeletal and ribbon silicates has been investigated[165] by pulsed polarisation and EPR. It has been shown that even very small amounts ($< 2 \times 10^{-2}$ wt.%) of organic free radicals have an appreciable influence on the electret charge and on the character of the EPR spectrum. The statement that there is a possibility of a low-temperature mechanochemical formation of free-radical states in polyorganosiloxanes is of particular interest in this connection[166]. The relaxation of stresses in the large helix of cyclolinear POSSO [121,140] can occur as a result of the rupture of a certain number of $\equiv$Si–O–Si$\equiv$ linkages[89] with formation of ionic[160] and free-radical states[166], which determine the intrinsic impurity content of the POSSO and to a large extent their electret capacity[165]. Inioc states are as a rule to a greater or smaller extent compensated either by external impurities or as a result of the interaction with traces of water:

$$\equiv Si^{\oplus} \quad \equiv Si{-}O^{\ominus} + \begin{matrix} O{-}H \\ | \\ H \end{matrix} \rightleftharpoons 2(\equiv Si{-}OH)\,.$$

Yet another cause of the formation of inhomogeneities in the structure of oligo- and poly-organosiloxanes may be hydrolytic OCS condensation side reactions due to the presence of impurities in the initial monomers. Admixtures of trichlorosilane can initiate gel formation under the conditions of the hydrolytic condensation of trichloromethyl- or trichlorophenyl-silane, whereas traces of chlorotrimethylsilane induce the effective termination of chain propagation, which is the reason for the necessity for the careful control of the quality of the monomers. A chromato-atomic absorption method for the determination of the above impurities in silicon tetrachloride has been proposed[167].

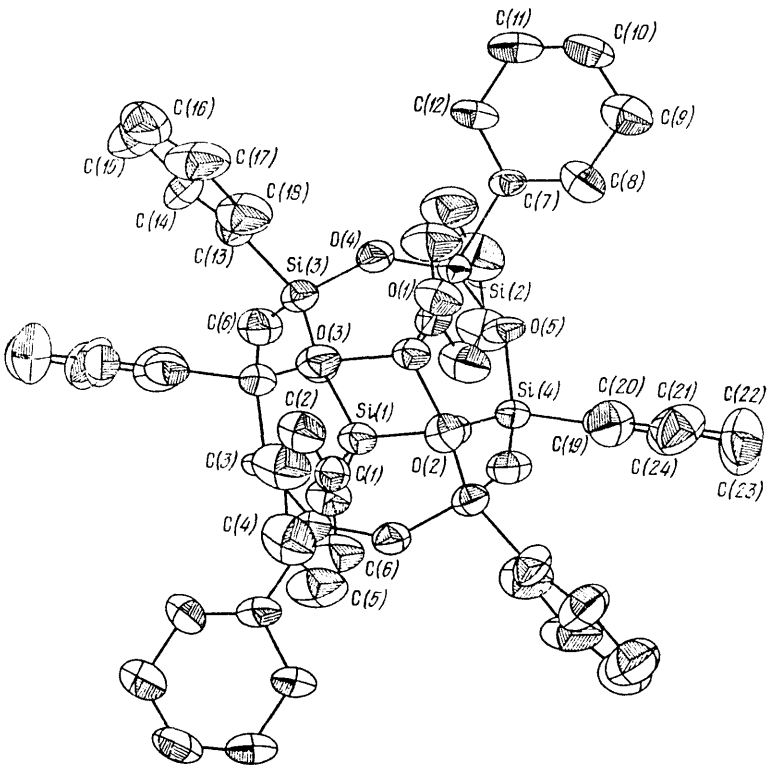


Figure 6. The structure of octaphenylcyclo-octasilasesquioxane $[RSiO_{1.5}]_8$ [projection along the Si(1)—midpoint of the Si(1′)Si(2′)Si(3′)Si(4′) face line]. Only the independent atoms have been numbered; Si(1′) denotes the atom linked to the Si(1) centre of symmetry[159].

Thus, in order to obtain a sufficiently pure product, meeting the requirements of electronic instrument making, it is essential that the reagents, including the solvents and water, be prepared carefully and also that suitable materials be selected for the technological equipment. Additional purification of the oligomer can be achieved by its reprecipitation from an appropriate solvent. However, it is difficult to hope for sufficiently complete elimination of alkali metal ions from the oligomer, since the ions apparently block some of the hydroxy-groups via ion-exchange reactions of the type

$$\equiv Si{-}OH + Na^{\oplus} \rightleftarrows \equiv Si{-}ONa + H^{\oplus}.$$

The above problem must therefore be solved also by other methods, for example, by limiting the mobility of ions by binding them in complexes with the matrix elements. It is known that for silicon dioxide this aim is attained by doping it with Al^{3+}, which results in the formation of capture centres. The energy characteristics of such centres, namely E_M = 0.50 ± 0.05 eV and H_H = 0.65 ± 0.09 eV, and their content (~1 × 10^{18} cm^{-3}) have been determined[168]. These data can serve as an approximate guide in selecting the lower limit of the content of the analogous centres in polyorganoaluminosilasesquioxanes, where the aluminium heteroatom has been introduced chemically into the siloxane chain[169].

7. Modification of OOSSO

Careful examination of the technology of the preparation and purification of OOSSO to make possible their use as dielectric materials in semiconductor electronics[108–111] led to the discovery of the special role of the phenomena on the surface of the support and in the immediate vicinity of the interface[108,170] of the solid phases, of the special significance of the presence and concentration of hydroxy-groups, traces of water, and limiting impurities, of the structure of the amorphous phase (in particular the ratio of the short-range and long-range disorders), and of the stresses arising both in the bulk of the amorphous films and at the interface with the support and in the support itself. Studies of amorphous and crystalline silicon dioxide proved productive for the elucidation of these problems. Studies of very thin films[171,172], both natural (grown by oxidising the surface of silicon) and deposited in a high-frequency discharge plasma, have in general not altered but merely refined the details of the picture of the boundary region illustrated in Fig. 1. One can actually state that silicon dioxide films with an increased content of carbonaceous impurities[173] and hydroxy-groups[17,174] or films formed under the decisive influence of water vapour[17,175] have come to be more vigorously

investigated during the last decade. This trend is associated with the fact that the presence of a limited amount of impurities, which do not greatly diminish the dielectric characteristics of the amorphous oxide, makes it possible to compensate for the disadvantages of SiO_2 discussed above. In this connection, investigations of the state of the OH groups in quartz[176] and silica[177], of the collective states for different modifications of SiO_2,[178-181] and of the structural defects in amorphous SiO_2 films on the surface of single crystal silicon[182] have developed greatly.

An important addition to all that has been said before about the SiO_2–Si reference system involves allowance for the stresses arising in multilayer structures. For example, a study has been made[183] of the influence of heat teatment on the stresses in amorphous silicon dioxide films deposited on a support by electron beam evaporation and a fairly old study[184] provided a general method for the estimation of internal stresses arising in multilayer structures. However, the study of the influence of the doping process on the relaxation processes in silicon dioxide layers is of greatest interest from the standpoint of the usefulness of the modification of siloxanes[185].

Silicon dioxide meets the principal requirements of electronics and electronic instrument making and is technologically convenient but is diffucult to modify. A material capable of competing with amorphous silicon dioxide should have effective dielectric properties, should be no less technologically convenient, and should be readily modified. These requirements are satisfied by structures based on POSSO.

(a) Modification of OOSSO by the introduction of a heteroatom directly into the siloxane chain. The modification of OOSSO by the introduction of Al, Ti, and Pb atoms into the siloxane chain in order to obtain polyorganoelementosiloxanes with improved dielectric characteristics different from those of POSSO has been described[111,128,169]. Aluminium heteroatoms were introduced in order to reduce the mobility of the alkali metal ions (mainly sodium ions), titanium atoms were introduced to increase the dielectric constant of the material, and lead atoms were introduced to reduce its permeability to accelerated ions[111]. The most important condition governing the modification was the retention of the non-crystallisability of the material over the entire range of its operating conditions (this was first observed for unmodified POSSO [89]).

There exist a series of methods for the introduction of the aluminium heteroatom into the siloxane chain. The preparation of oligomeric alumino-organosiloxanes by the reaction of aluminium compounds (for example, aluminium isopropoxide) with α,ω-dihydroxyorganosiloxanes having the general formula HO[RR'SiO]OH, where R = methyl and R' = methyl or vinyl, formed via a reaction, involving the opening of the ring in the corresponding organocyclosiloxanes with an alcoholic solution of alkali[128] followed by the neutralisation of the products with acetic acid, is technologically the most convenient. Depending on the reactant ratio and the nature of the siloxane diols employed, different oligo-organoaluminosiloxanes have been synthesised: oligodimethylaluminosiloxanes with the silicon : aluminium ratios g = 4, 8, and 12; oligomethylphenylaluminosiloxanes with g = 1.8, 2,4, 3.6, 4.25, and 13.2; oligomethylvinylaluminosiloxane with g = 12. The reaction scheme, for example, in the case of an equimolar reactant ratio, is

$$Al(OC_3H_7)_3 + HO-[-SiRR'-O-]_n-H \rightarrow -\overset{\displaystyle OC_3H_7}{\underset{|}{Al}}-[-OSiRR'-]_n-O- \ .$$

Linear oligomers are formed, which is confirmed by the presence of an infrared band with $\bar{\nu}$ = 1130 cm^{-1}, caused by the vibrations of the C–O bond in the isopropyl group. With increase of the relative amount of siloxanediol, i.e. in the presence of an excess of Si–OH groups, this band disappears, which is associated with the formation of network oligomers. It is significant that oligomers without hydroxy-groups are formed in this case, which follows from the absence of the characteristic infrared absorption bands in the range 3200–3600 cm^{-1}.

Consequently in the aluminium isopropoxide–siloxanediol system there is a possibility not only of heterofunctional cocondensation but also homofunctional cocondensation of siloxanediols, catalysed by aluminium compounds, takes place. The oligomers formed are readily soluble in organic solvents.

Films of oligo-organoaluminosiloxanes (OOASO) have been obtained[128] from toluene solutions on glass, silicon, and steel supports. The polymerisation was carried out by heat treatment and was accompanied by the loss of fusibility and solubility of the films. The rigidity of polyorganoaluminosiloxane films increases with decrease of the ratio g.

Satisfactory coatings are obtained on the basis of MM-12, MV-12, and MF-13.2 varnishes.

A stronger intermolecular interaction in polyorganoaluminosiloxanes compared with POSSO has been established[128] and has been confirmed by infrared spectroscopic data. It is associated with the presence of the aluminium atom in the siloxane chain. The dielectric parameters of polyorganoaluminosiloxanes satisfy the requirement that their functionality be high while retaining the non-crystallisability characteristic of OOSSO. In addition, polyorganoaluminosiloxanes are characterised by the reduced mobility of alkali metal ions compared with POSSO and SiO_2, which makes it possible to reduce appreciably the time drift of the parameters of silicon semiconductor devices.

The method of preparation of modified OOSSO by the synthesis of spiro-compounds, whose range is apparently largely limited to compounds of Group IV elements, for example, titanium-containing compounds, is promising[186].

In principle, there is a possibility of other procedures for the synthesis of oligo-organoelementosiloxanes: the synthesis of reactive monomers incorporating a heteroatom[109-111,187,188] and the interaction of OCS with the oxides and hydroxides of elements under special conditions (for example, a study has been made[189] of the interaction of TCMS with titanium dioxide in a fluidised bed). However, such processes are less selective than the specific synthesis of oligomers with a heteroatom in the siloxane chain and can lead to oligomers incorporating a heteroatom both directly in the siloxane chain and in the surrounding groups.

(b) Modification of OOSSO by the introduction of a heteroatom into the groups surrounding the siloxane chain. Numerous studies surveyed in monographs[48-50,52,92,190] and others[83,96,191,192] were devoted to the influence of the groups surrounding the siloxane chain on the properties of polyorganosiloxanes (POSO). The vast majority of such investigations involve the replacement of the alkyl group by an aryl or alkoxy-group. Such modifications of the surrounding groups are undesirable, since they involve an increase in the relative content of carbon which constitutes a limiting impurity in the dielectric–single crystal silicon (germanium) structures, which one attempts to avoid as far as possible in the formation of metal oxide films and coatings[16].

More homogeneous materials with a better distribution of modifying heteroatoms can be obtained by opening three-dimensional cyclic structures of the type of T_8, T_{10}, or T_{12} with formation of compounds having a ladder (double stranded)

structure[53] with the simultaneous introduction of organometallic compounds, tetrabutoxytitanium[36,83], tetraethoxysilane, etc.[165,193], which add to the non-bridging oxygen atoms. The influence of the metal on the siloxane chain via an oxygen atom is localised in mono- and oligo-elementosiloxanes in the vicinity of the M–O–Si group[161]. The oligomers formed in this way retain their capacity for polymerisation and the corresponding polymers, while possessing the specified dielectric characteristics, retain their non-crystallisability characteristic of POSSO.

(c) Modification of POSO by chemical doping. The method of chemical doping makes it possible to alter sharply the characteristics of polymers using comparatively small amounts of dopants and additives, imparting to such polymers and the materials based on them special properties necessary for specific applications[194,195]. It is know that in the thermal and thermo-oxidative stabilities of polydiorganosiloxanes increase appreciably after the introduction of a series of heteroatoms into the main chain[50,196]. A similar effect can be achieved also by the introduction into the polymer matrix of certain low-molecular-weight siloxanes[197] or elementocyclosilazanes (for example, those containing the titanophosphinate group), whose effect apparently consists in the formation of rare interchain cross-links. Even when their concentration is very low, such cross-links alter the properties of the polymer, which can no longer be regarded as linear; its thermal stability, mechanical properties[198], and electrical strength are changed.

When the POSSO has already been formed, this mechanism cannot operate and chemical doping is carried out in the stage involving the formation of an oligomer film by introducing small amounts of organometallic or organic compounds which react with the oligomers and are incorporated in the polymer matrix in the course of hardening[165,193]. This method makes it possible to control within certain limits the electrophysical and particularly the electret characteristics of the materials. In this case, apart from the formation of additional cross-links between the elements of the helix or between the cyclolinear chains of the polymer, the additives can be incorporated into the groups surrounding the main chain. The relative contributions of these processes are determined both by the conditions governing the introduction of the additives and by the conditions in the hardening of the polymer.

As in the doping of semiconductors[3], the POSSO chemical doping processes involve a fundamental difficulty associated with the limited capacity of the matrix, i.e. the fact that it can incorporate in its structure not more than a strictly specified amount of the dopant. Beyond these limits, phenomena, which as a rule vitiate all the advantages achieved by the modification of the initial matrix, take place. It is difficult to say what constitutes the starting point of the impairment of the material: the appearance of presegregations of a new phase or the breakdown of the sections of the matrix adjoining directly the regions of the support with an electric field gradient (surface defects, charged impurities, outcrops of dislocations on the single crystal surface)—it is difficult to separate these two processes in time. This is followed by the appearance of discontinuities in the matrix with segregation of the impurity along the boundaries of the macroblocks, analogous to those described by Spektor[199], and finally crystalline or amorphous inclusions of the independent phase of the dopant or the products of its reaction independent of the matrix are formed. Under the conditions of doping at concentrations far outside the limits of the chemical capacity of the matrix, all these effects operate simultaneously[193].

The modification procedures enumerated above, in particular chemical doping, depend greatly on the conditions governing the conversion of the OOSSO into the corresponding polymers and also on the chemical nature of the oligomers and modifying agents employed.

IV. OLIGOMER POLYCONDENSATION PROCESSES

In view of their instability (tendency towards structure formation in both the solid state and in solution)†, oligoorganosilasesquioxanes are of no practical value.

In order to convert these intermediates into the finished materials, it is necessary to convert the oligomers into the corresponding high-molecular-weight products. The general characteristics of the polycondensation of OOSSO have been examined in a number of studies[49,50,52,53,78,89,90,92,119,129,275]. In the heat treatment of oligomers, one can arbitrarily distinguish two stages of the process. The first stage develops in the oligomer melt at temperatures in the range 70–120 °C [depending on the molecular weight (M_{OOSSO}) and on the MWD of the oligomer]. The second stage takes place in the solid phase after hardening. Competing reactions are polycondensation involving hydroxy-groups and ring opening. In fact the temperature ranges of these reactions overlap to only a slight extent—the first reaction is almost completed after the attainment of 200 °C, while the second reaction is only beginning at these temperatures. However, both reactions influence the formation of the structure of the POSSO matrix. Taking into account the data on the structure of amorphous silica[157], it is necessary to postulate the presence of residual hydroxy-groups in POSSO up to temperatures exceeding significantly that of the thermal or thermo-oxidative elimination of hydrocarbon groups[120]. The presence of residual hydroxy-groups in the POSSO matrix plays an important role in the interaction of POSSO with the supports[108]. Low-molecular-weight compounds of the type of T_8 and other three-dimensional cyclic compounds undergo thermal polymerisation with difficulty. Catalytic reactions with ring opening[53] of the type of the polymerisation of cyclic oligomers with $F = 2.0$ [145,147,201] or cross-linking under the influence of high-energy radiations[57,110,111], are more characteristic of these compounds.

The process which is more likely to take place in the solid phase under the influence of high temperatures[202] involves the elimination of organic groups, which leads to the formation of a material whose properties are similar to those of silicon dioxide[120]. However, the purity of this material, obtained under the usual conditions in bulk, is greatly inferior to that of silicon dioxide obtained by fusing quartz, by the oxidation of the surface of silicon, and even by the decomposition of tetraethoxysilane or other organosilicon monomers. This is associated with the fact that the thermal degradation of polyorganosiloxane, like that of polyorganoelementosiloxanes[203], entails the segregation of a new phase in the form of a cluster or colloidal carbon or of graphite inclusions accompanied by the darkening of the material. High-energy radiations (ultraviolet radiation, X-rays, and neutron, electron, and proton beams) have an effect similar to high temperatures as regards the degradation of the polymers.

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†An exception to this rule is provided by cyclic three-dimensional compounds, for example, octaorganocyclo-octasilasesquioxanes, which form an independent subclass of silasesquioxanes[200], but these also have poor mechanical properties.

The influence of ultraviolet radiation in the region of 265 and 420 nm and of proton beams with an energy of 500 keV on POSSO has been investigated[204,205] as a function of the organic group and it was shown in particular, that the replacement of 27–50 mole % of the methyl groups in PMSSO by phenyl groups increases appreciably the radiation stability of the polymers. The resistance of the organic groups, particularly phenyl groups, to the action of temperature and irradiation can be significantly increased by introducing into the organosiloxane matrix transition metals or other complex-forming fillers[206–209].

The preparation from POSSO of a material whose composition is identical to that of silicon dioxide, which is essential for applications in electronics, becomes possible in the thermo-oxidative annealing of thin (up to 1 μm) PMSSO films with $F \geq 3.0$.[120] In this case the process *in vacuo* can be described by the overall equation

$$\{H_3CSiO_{1.5}\}_n + 3n/2\,O_2 \rightarrow \{SiO_2\}_n + nCO + 3n/2\,H_2O\ .$$

Volatile reaction products leave the film without causing breaks in its continuity. The process leads to the formation of new siloxane linkages, giving rise to interchain cross-links.

In studying the temperature dependence of the polycondensation mechanism, one must take into account the fact that, as shown, in particular, in the study of Andrianov et al.[108], the heterolytic mechanism of the cleavage of siloxane linkages predominates at moderate temperatures (up to ~400 °C):

$$\equiv Si{-}O{-}Si\equiv \rightleftarrows Si^{\oplus} + \equiv Si{-}O^{\ominus}\ ,$$

while at higher temperatures (above 400 °C), the homolytic mechanism predominates:

$$\equiv Si{-}O{-}Si\equiv \rightleftarrows \equiv\dot{S}i + \equiv Si{-}O^{\cdot}\ .$$

The low-temperature hardening of siloxanes is accelerated by ionic catalysts[144,146,210]. The coexistence of various polycondensation mechanisms can be illustrated by the results of its determination of the rates of hardening of thin oligomer films on various supports (Fig.7).

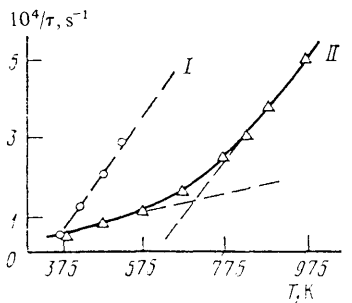


Figure 7. Dependence of the rate of hardening of oligomethylsilasesquioxane on different supports: I) on a metal; II) on single crystal silicon.

The knowledge of only the general characteristics of the polycondensation of OOSSO is insufficient for the development of processes leading to the formation of dielectric films and coatings directly on the surfaces of any semiconductors.

For a better understanding of the problems arising in the development of such materials, we shall list the main requirements which they must meet:

(1) Dielectric properties not inferior to those of amorphous silicon dioxide ($\varepsilon \cong 3.0$; $\tan\delta \cong 1 \times 10^{-2}$; the number $n_{por} < 5\ cm^{-2}$; $E_{br} > 1 \times 10^6\ \Omega\ cm^{-1}$; $\rho_V > 1 \times 10^{14}\ \Omega\ cm$; $Q_V \cong 5 \times 10^{11}$ e.s.u. of charge per cm^2; $\mu_M^{POSSO} \cong \mu_M^{SiO_2}$).

(2) The maximum attainable layer and surface homogeneity in the absence of any inclusions of another phase.

(3) Minimal stresses both in the bulk of the dielectric film and at the interface with the semiconductor.

(4) Maintenance of the concentration of the surface states of the protected semiconductors at the initial level and if possible its reduction.

(5) Resistance to the action of corrosive media (NH_3, PH_3, AsH_3, etc.), moisture, and solvents.

(6) Resistance to the action of accelerated ions.

(7) Capacity for being modified within fairly wide limits at least as regards ε and Q_V ($2.0 < \varepsilon < 15$; $1 \times 10^{10} < Q_V < 1 \times 10^{14}$) with retention of other dielectric characteristics at a fairly high level.

(8) Capacity for being etched with standard solvents at rates v_{etch} comparable to $v_{etch}^{SiO_2}$ and capacity for being modified as regards v_{etch}.

Naturally no one material can meet all these requirements simultaneously. It is necessary to create a series of materials of one class obtained by isotypical technological processes.

Dielectric materials likely to be useful in electronics and instrument making have been developed in a series of studies[36,55–57,70–75,83,86,88,89,99,107–112,118,120,128,140,160,165,169,170,193,194,211,212,275] in conformity with these requirements on the basis of comprehensive investigations of the relation between preparation and conversion conditions and the molecular and phase structure of the products with control of the physicomechnical and electrophysical characteristics.

Homogeneous oligomers free from particles of a heterophase (gel) are obtained in a total displacement flow reactor with parallel injection of the components. A broad MWD complicates the technology of the hardening of the oligomers. Fusion within wide temperature limits results in the existence of the oligomer in the form of a two-phase system throughout some time from the beginning of the process. Reactions in the liquid phase are faster than in the solid phase, so that polymerisation in the melt is completed, while part of the oligomer has still not fused and, by the time when the residual oligomer has melted and begun to polymerise, the head fraction has already solidified. Furthermore, the polymerisation conditions near the upper limits of the fusion temperature range differ from the initial conditions, which creates an additional inhomogeneity and stresses in the films. It has been noted[78,90] that larger oligomeric seeds create a more defective structure.

Under the conditions of a wide MWD, the growth of large helices is hindered, the alternation of helical and xonotlitic structures becomes possible[99] and the presence of such comparatively small ribbon inclusions can reduce the electrical strength of the material. Thus, in order to obtain high-quality dielectric films based on POSSO, it is preferable to have an oligomer with the narrowest possible MWD (in the limit, individual oligomeric molecules) and this dictates the necessity to optimise the synthesis of the OOSSO with respect to the MWD.

In order to obtain the composites and press-materials based on OOSSO, some of the solvent is left in the oligomer as a binder before the final polymerisation stage. This ensures more effective mixing and moulding of articles and also reduces the adhesion of the composites to the press-moulds.

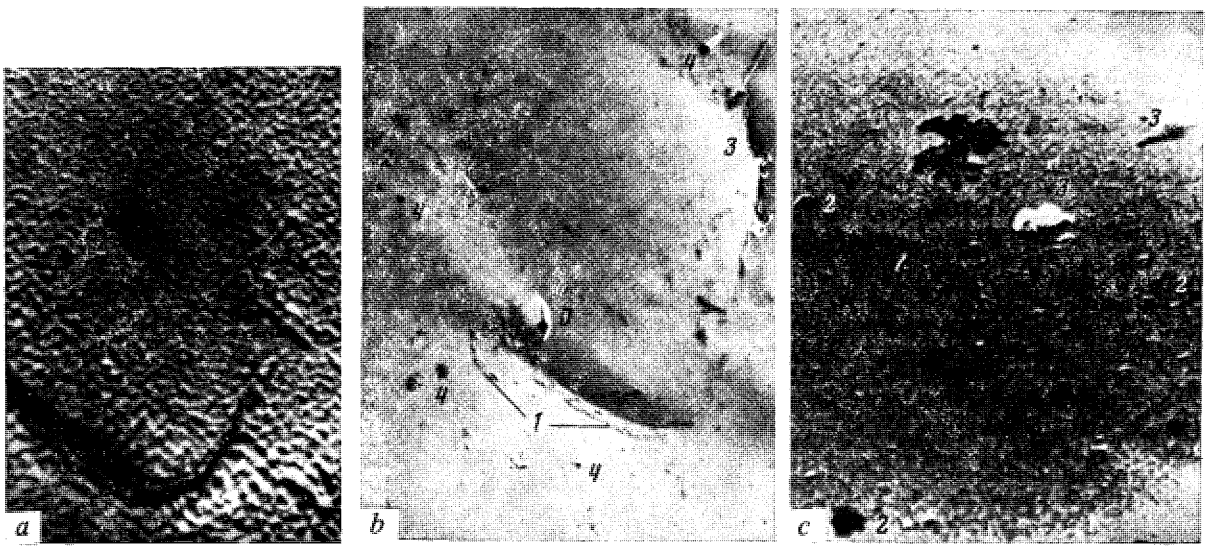


Figure 8. Comparison of the structures of regions of polymethylsilasesquioxane and amorphous silicon dioxide films (×420) which have undergone electrical breakdown[120,140]: *a*) ideal surface of PMSSO film with different thicknesses; *b*) breakdown of the ideal PMSSO film (the Al electrode is deposited on top) on single crystal silicon (10 breakdown steps in one region with restoration of electrical stability after 9 cycles); *O*—centre of breakdown crater; 1) surface fusion of the material of the electrode along the breakdown trajectory; 2) breaks in the Al electrode with surface fusion associated with surface electrical breakdowns; 3) massive breaks in the Al electrode associated with electrical breakdown by reverse currents; 4) satellite punctures in the Al electrode; *c*) electrical breakdown of a film of amorphous silicon dixoide (the Al electrode is deposited on top) on single crystal silicon (single electrical breakdown): 1) breakdown crater; 2) satellite breaks on the periphery; 3) ejected surface-fused material of the electrode.

When thin films are formed over a large area, this method is unsuitable because numerous defects (for example, large and small open and closed bubbles) are formed on the surface of the film in this instance; they are produced when the solvent and the water formed in the polycondensation process are removed. Although such shallow defects do not influence the integral dielectric properties of the moulded POSSO films, they can prove to be weak sections in local electrical breakdown. Hardening is therefore carried out under controlled conditions[120,128,140] ensuring the removal of the solvent and condensation of water through the surface of the film.

The dielectric layers formed in this way and based on polymethylsilasesquioxane, polyphenylsilasesquioxane, and other POSSO [89,108–112,120,140] are distinguished by homogeneity throughout their bulk and an even surface (Fig.8*a*) with average dimensions of the rugosities (of the type of spherical growth formations) smaller than for thermo-oxidative silicon dioxide[213] and with smaller ejections of the dielectric material on repeated electrical breakdown than in the case of a single electrical breakdown of an SiO_2 film (8*b* and 8*c*).

Unfortunately direct control of the OOSSO polycondensation processes on the protected surfaces is difficult to achieve by traditional methods in view of the small thickness of the films formed. However, bearing in mind the initiating effects of the point defects in a silicon single crystal[108], one can employ the results of the study of these processes on specimens of the free oligomer.

The weight loss effects and thermal phenomena in the polycondensation of a number of oligomers have been investigated[214].

V. PROBLEMS OF THE INTERACTION OF OLIGO- AND POLYORGANOSILASESQUIOXANES WITH A SOLID HETEROPHASE

The first applications of POSSO with high functionality were associated with their thermal stability and hydrophobic properties. Parameters of the materials such as their resistance to high temperatures and ionising radiations[202–205,209] and corrosive media[215–217], mechanical characteristics[198] and low cost achieved by a wide variety of procedures for the preparation of binders[71–73,107,218–222] and composites based on them[223–229] were also of decisive importance at this stage. In this first stage of research, compositions with interesting electrophysical[55,152,190] and electronic[229] characteristics were already obtained. Studies involving the investigation of the mechanisms of the interaction of reactive monomers[133,189, 192,230–233] and oligomers[133,233–236] with the solid phase of the filler (textile fibres, silicates and cements, silica gel, and aerosils), taking into account the functionality of the groups on their surfaces[236,237], may be regarded as the next stage. Finally, the general postulates concerning the interaction at the interface between two solid phases, one of which is an organosilicon dielectric, were formulated[108,170] on the systemtic basis of ideas concerning the transition layer in semiconductor–dielectric and metal–dielectric systems[7,8,13,35,36, 238–240] and the structure of the surface layers of amorphous element–oxygen solid phases[160,180,241], as well as experimental data obtained for the organosilicon dielectric–silicon and organosilicon dielectric–metal systems[54,56,109–111,120,128,129,140, 151,165,169,193,212].

1. Blended Compositions Based on Organosilicon Binders

Problems concerning the formation of compositions filled with glass fibre and their characteristics have been described comprehensively in the literature[47–53,92,190], so that in the present section we shall therefore consider only individual examples of blended compositions based on organosilicon binders (OSB) [71,107] which are of interest either as regards their applications or from the standpoint of the general characteristics discovered.

The possibility of employing organosiloxanes in the electrotechnical industry for the formation of insulating layers and enamels having an improved heat resistance, and reduced flammability and with a low evolution of toxic volatile substances was first examined by Schwarz[129]. A number of studies have been devoted to problems of the thermal stability of composites based on filled polyorganosiloxanes[206–209,223,224]. It has been noted that the thermal stability of polyphenylsilasesquioxanes filled with metals increases as a function of the filler metal in the sequence Pb < Fe < Ni < Bi < Cd < Cu < Co. The activity of the metal is determined not only by its chemical nature but also by its degree of dispersion, which has been confirmed in relation to the composite of OSB and iron carbonyl powder[226].

A report[223] describes the creation of a series of thermostable and corrosion-resistant dielectric compositions based on oligomers obtained by the hydrolytic condensation of OCS (TCMS, trichlorophenylsilane, and dichlorodimethylsilane) in the presence of iron(III) chloride and zinc or aluminium dust or titanium dioxide as fillers and the possibility of modifying varnish compositions by means of organic solvents and by adding a polyester (in the case of hot hardening: 2 h at 180–200 °C) or an alkyl resin (in cold hardening; 2 h at room temperature) was examined. Another report[224] is devoted to a comparative study of the characteristics of enamels made from these composites placed on steel supports. For satisfactory dielectric parameters, the best thermal stability is shown by the polymethylphenylsiloxane enamel with zinc dust and the greatest chemical stability and resistance to the atmosphere is shown by an enamel with the rutile titanium dioxide phase modified with 20 wt.% of polyester.

The definite structural similarity between POSSO, particularly those obtained under specific conditions[99], and silicates with large cations[154,155] was already mentioned previously. The study of the interaction and structrual transformations in POSSO composites with iron-containing chrysotile-asbestos[227] and OSB with fluorophlogopite[228] is of definite interest in this connection. The first composition is of special interest, since the supermolecular organisation of chrysotileasbestos, having the formula $Mg_6[Si_4O_{11}].(OH)_6.H_2O$, belongs to an extremely rare type of tubular crystals and agrees well with the helical organisation of POSSO.[140] Furthermore, it can be seen from the formula that this mineral contains a large amount of active hydroxy-groups and, in view of its intrinsic low (mainly ionic) electrical conductivity and capacity for cocondensation via the hydroxy-groups with OOSSO, this ensures a high thermal stability and effective dielectric characteristics of the composite[227].

The most striking result in the application of blended OSB composites with a filler in electronic instrument making has been achieved in the study of photocapacitive characteristics of inhomogeneous structures consisting of dispersions of photoconducting microcrystalline cadmium sulphide particles in an organosilicon varnish[229]. The possibility of developing photovaractor elements for the frequency range 10^3–10^6 Hz for illumination intensities of 10^{-2}–10^3 lm with a maximum overlap coefficient of ~5 has been demonstrated experimentally.

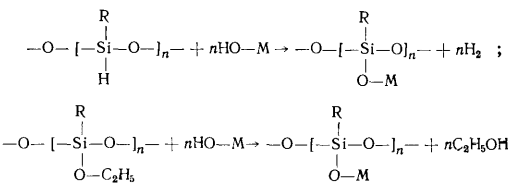
2. Cocondensation of Mono-, Oligo-, and Poly-Organosiloxanes with Functional Groups on the Surface of a Solid Phase

The interface formation processes in the reaction of mono-, oligo-, and poly-organosiloxanes with amorphous or polycrystalline oxide phases are fairly complex. In this case the structure of the phase of the support "dictates" the structure of the junction boundary, as shown in a study[241] in which the author emphasises the decisive role of the short-range order of the formation of the surface layer in the molecular deposition of oxides layer by layer using the principle of the isoenergetic state of oxygen, characterised in any solid stable oxides by the approximately constant overall bond energy $E_{E-O} \cong 240$ kcal g-atom^{-1}. A calculation (tested experimentally) has been carried out by the extended Hückel–Hoffman method specifically for the [SiO_4] tetrahedron in SiO_2 and led to the following results: charge on the oxygen atom $N_O = -0.93$; population (total order) of the Si–O bond $P_{Si-O} = 0.539$; bond energy $E_{Si-O} = 104.3$ kcal mol^{-1}; π-bonding ~16%; coordination number $k = 2$; overall electron population of the oxygen bond in the silicon dioxide lattice $kP_{Si-O} = 1.078$, i.e. $kP_{E-O} \cong 1$ as in other stable oxides. These conclusions are in good agreement with the results of a study[180] where data for the splitting of the optical frequencies in the spectra of amorphous bodies led the authors to the conclusion that the influence of the orientation of the silicon–oxygen tetrahedra makes a small contribution and that account must be taken of the long-range effect by introducing a term related to the Coulombic forces determined by the presence of effective charges on the silicon and oxygen atoms. The state of the hydroxy-groups on the surface of the oxide has been investigated in detail[241] and the cause of the difference between the states of the hydroxy-groups on the surfaces of aerosils and quartz glass with [SiO_4] octahedra, on the one hand, and silica gels and silicic acid hydrogel with [SiO_6] hexahedra, on the other, was discussed. In this case the difference is caused by the binding of the OH group to the nearest silicon atom, whose state also depends on the coordination. The conclusion[241] that there are different states of the OH groups on the SiO_2 surface has been confirmed by the preparation of aerosils with isolated amino-groups on the surfaces[237].

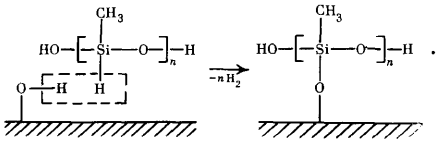
These studies, carried out on simple objects, permit at least a qualitative understanding of the processes occurring on the surfaces of materials related to polyorganosiloxanes[134, 233,235,236].

It has been shown that the interaction of polydimethylsiloxane rubbers with aerosils proceeds via the silanol groups[236], which is confirmed by the different behaviour of rubbers with free and blocked terminal silanol groups. However, physical interaction forces nevertheless play a decisive role in the above system, which is manifested by a decrease of the content of the polymer bound to aerosil at temperatures in excess of 200–240 °C. On the other hand, when the surface of highly dispersed silicon dioxide was modified by low-molecular-weight silazanes and siloxanes, the formation of a chemical bond between the surface of silicon dioxide and the compound employed was established[134]. It has been shown[34] that the different interactions of the organosilicon monomer and oligomers[233] with Portland cement having the composition (wt.%) 22.06 SiO_2, 3.98 Fe_2O_3; 3.89 Al_2O_3, 63.9 CaO, 2.68 SO_3, 1.65 MgO, 1.42 H_2O, and 0.27 Na_2O and its fully hydrated (to the extent of 99.9%) modification is determined mainly by the relative contributions of two processes: chemical reaction involving the active groups (Si–H, Si–OH, and Si–OR) and adsorption. The products of the chemical reactions were identified chromatographically[233]. For example, the presence of molecular hydrogen and ethanol in the products is attributed to the occurrence

of the following processes:



The detection of molecular-hydrogen is particularly important, confirming the mechanism proposed by Reikhsfel'd et al.[234]:



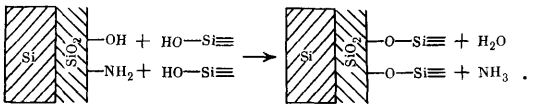
According to this mechanism, the terminal hydroxy-groups of the oligomer are retained and can participate in the subsequent polycondensation or cocondensation with epoxide resins. Although the result of the analysis of the reaction products for molecular hydrogen is not quoted in the above study[234], the proposed mechanism has been confirmed by other data[233].

3. The Mechanism of the Interaction of Oligo- and Polyorganosiloxane with the Surface of Single Crystal Silicon and the Possibility of the Polymerisation Filling of Polyorganosilasesquioxanes

It was noted above that among polyorganosiloxanes, the best dielectric characteristics, not inferior to the characteristics of amorphous silicon dioxide, are those of polyorganosilasesquioxanes with $F \geq 3.0$ and small substituents, as a rule methyl substituents. PMSSO have therefore found applications in semiconductor devices and integrated circuits as passivating films, active dielectric layers, protective coatings, and masks in doping processes[56,108,110,111]. The advantages achieved by employing POSSO are associated not only with the simplification of the technology of the formation of the layers and films directly on the surface of the semiconductor single crystal and with their non-crystallisability[89, 110,111] but also with the possibility of the passivation of the surface of a single crystal when the latter interacts with POSSO as a result of the decrease of the concentration of the surface states (of the type of surface impurities and point defects). The phenomenon is caused by the occurrence of a complex set of chemical reactions on the surface of the single crystal.

We may recall that in the single crystal silicon–amorphous silicon dioxide system there is a transition layer at the interface, which is completed by a thin layer of the natural oxide growing on the surface of the silicon single crystal at room temperature in air. The thickness of this layer varies in the range 15–30 Å as a function of the material of the single crystal and external conditions. The nature of the interphase states is determined by the supersaturation of the surface layer of the single crystal with oxygen, the presence of stresses due to the incompatibility between the surface layer subjected to stretching stresses and the pseudocoesite layer subjected to compressive stresses, as well as the presence of microcrystallite inclusions and discontinuities in the intermediate $SiO_x (x < 2)$ layer. Furthermore, the concentration of the interphase states increases appreciably due to the presence on the single crystal surface of interstitial silicon atoms—adatoms, vacancies, and their clusters[108] and also as a consequence of the presence of hydroxy-groups and other functional groups (for example, NH_2) and impurities sorbed on the silicon dioxide surface. The influence of the interphase state on the electronics of the semiconductor–dielectric structures has been described in detail in the literature[151]. The self-limited ordered clusters examined in Section II [20] have structures very similar to those of POSSO and the stresses arising in the transition region may partly relax as a result of the cleavage of the Si–O bond via a free-radical mechanism[166].

On the basis of the data described above, we shall consider the mechanism of the interaction of PMSSO with the natural oxide film. The interaction with the oligomer melt begins from the oxide surface via the functional groups[169] in accordance with the scheme



The removal of volatile reaction products from the surface layer does not present difficulties under these conditions. The next stage, initiated by free-radical states present in the pseudocoesite layer, consists in the incorporation of the substance of this layer in the polymer matrix, which is accompanied by an increase of the overall functionality of the material. Bearing in mind the ratio of the amounts of the interacting OMSSO and the amorphous silicon dioxide, which can be readily found from the relative thicknesses of the layer—on average a ~20 Å SiO_2 layer (including the ~10 Å SiO_x layer with $x < 2$) and a $\sim 5 \times 10^4$ Å OMSSO layer—it is easy to understand why the overall increase of functionality is small.

The next, concluding stage is associated with the polycondensation of the oligomer at 180–200 °C and the formation of an infusible and insoluble skeletal polymer on the surface of the support. The processes involving the incorporation of a silicon dioxide layer in the overall polymer structure are completed in this temperature range and there is a sharp decrease of the concentration of hydroxy-groups. The inter-relation of the oligomer–polymer–synthetic silicon dioxide (from the polymer)–fused quartz structures and the character of the reactions can be seen from a comparison of their infrared spectra illustrated in Fig.9. The presence of a small but finite number of hydroxy-groups in the polymer formed ensures the possibility of the generation at temperatures below 200 °C of ionic states in the relaxed POSSO matrix and of the competition between heterolytic and homolytic silanol bond dissociation processes at temperatures of 200–400 °C; above 400 °C, the latter process becomes dominant[108]. These processes are described by the equations of the formation reactions of ionic states:

$$\equiv Si{-}O{-}H \rightarrow \equiv Si{-}O^{\ominus} + H^{\oplus} ,$$
$$\equiv Si{-}O{-}H \rightarrow \equiv Si^{\oplus} + HO^{\ominus} ,$$

and free-radical states:

$$\equiv Si{-}O{-}H \rightarrow \equiv Si{-}O^{\cdot} + H^{\cdot} ,$$
$$\equiv Si{-}O{-}H \rightarrow \equiv \dot{Si} + HO^{\cdot} .$$

The terms "ionic state" and "free-radical state" imply that the charge or the unpaired electron on the silicon or on what have become non-bridging oxygen atoms are bound and localised in a certain element of the matrix[108] and their movement involves the mechanism of the exchange interaction with the nearest neighbours[160,170]. The non-chain products of the cleavage of the silanol bonds, namely HO°, H°, $HO^{\cdot}$, and

H$^{\cdot}$, are not localised, possess a definite mobility in the siloxane matrix, and are capable of interacting with POSSO via a mechanism involving ring opening[108,170]:

$$\equiv Si-O-Si\equiv + HO^{\ominus} \rightarrow \equiv Si-O^{\ominus} + \equiv Si-OH \ ,$$
$$\equiv Si-O-Si\equiv + H\dot{O} \rightarrow \equiv Si-\dot{O} + \equiv Si-OH \ ,$$
$$\equiv Si-O-Si\equiv + H^{\oplus} \rightarrow \equiv Si^{\oplus} + \equiv Si-OH \ ,$$
$$\equiv Si-O-Si\equiv + H^{\cdot} \rightarrow \equiv \dot{S}i + \equiv Si-OH \ .$$

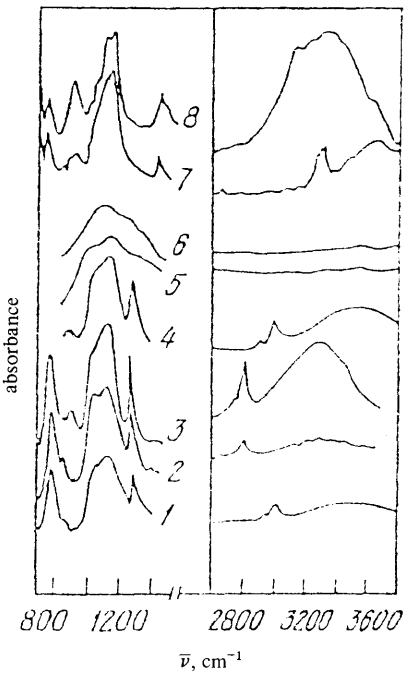


Figure 9. Comparative infrared spectroscopy of polyorganosilasesquioxanes, synthetic silicon dioxide, and fused quartz[89,110,111,120,275]: 1)–3) OMSSO, $F = 3.25$, $F = 3.14$, and $F = 3.0$ respectively; 4) PMSSO, $F = 3.0$ (prepolymer); 5) PMSSO annealed in air at 700 °C for 1 h; 6) fused quartz; 7) octaphenylcyclo-octasilasesquioxane; 8) tetrahydroxy-tetraphenylcyclotetrasiloxane.

Bearing in mind that the macroscopic mobility of fragments of the three-dimensional siloxane chain in which the ionic or free-radical states are localised is zero at a concentration of hydroxide ions or hydroxy-radicals $c_{HO^{\ominus}} \leq a$ or $c_{HO^{\cdot}} \leq b$ (whereupon the probability of their recombination is low), one may assert that, up to a certain consideration limit, the processes involving the generation of ionic or free-radical states in the matrix predominate over their recombination processes.

The structural defects on the surface of a dislocation-free silicon single crystal are point defects of the type of interstitial atoms, vacancies or their clusters. We shall examine only individual defects, which does not alter the overall picture. In the case of a simplified model of a section of the single crystal silicon surface with two point defects—a vacancy and an interstitial atom—it has been estimated that the long-range influence of these defects in the POSSO matrix extends over more than 54 Å [108] on the basis of the data of Panteleev and Opulich[242], which in the case of polyphenylsilasesquioxane, with the interchain distance $d = 12.8$ Å,[89] covers, in the direction at right angles to the interface, more than four molecular layers and, for PMSSO with $d = 8.4$ Å, more than six molecular layers.

The silanol bonds may be cleaved under the influence of the gradient of the electromagnetic field of the point defects consisting of an interstitial atom or a vacancy (similarly to the situation discussed in the study of Vorotyntsev and Kornyshev[240]). The gradients of the electromagnetic field of point defects constitute at the same time the driving force of the migration of the ionic and free-radical states in the organosiloxane matrix. Bearing in mind the paramagnetism of the vast majority of the single crystal silicon surface states considered, their interaction with the ionic states emerging at the interface has been shown[108] to take place as a result of charge transfer:

$$\equiv Si-O^{\ominus} + \{R^{\pm}\} \rightarrow \equiv Si-O^{\cdot} + \{R^{\pm}\cdot\bar{e}\} \ ,$$
$$\equiv Si^{\oplus} + \{R^{\pm}\cdot\bar{e}\} \rightarrow \equiv \dot{S}i + \{R^{\pm}\} \ ,$$

where $\{R^{\pm}\}$ represents a semiconductor in the form of an infinite donor–acceptor reservoir relative to a single ion.

The charge transfer results in the formation of localised free-radical states capable of interacting, following a sufficiently close approach to the interface, with the unpaired electrons localised at the defects. Very few charged surface states interact directly with the ionic states emerging at the interface.

As free-radical states of the type $\equiv Si-O^{\cdot}$ approach an interstitial silicon atom on the single crystal surface, there is a possibility of its multistage interaction with three uncompensated bonds, which can be described by the following overall expression:

$$3\,(\equiv Si-O^{\cdot}) + A\{M\} \rightarrow \begin{matrix} \equiv Si-O \\ \equiv Si-O \\ \equiv Si-O \end{matrix} \!\!> Si-\{M\} \ , \qquad (3)$$

where A{M} is an interstitial atom (Si) on the surface of the single crystal {M}, which will be henceforth referred to as an adatom.

The interaction of a free-radical state of the type $\equiv \dot{S}i$ with a point defect of the type of a vacancy V{M} can be described analogously:

$$\begin{matrix} \equiv Si-O \\ \equiv Si-O \\ \equiv Si-O \end{matrix} \!\!> \dot{S}i + V\{M\} \rightarrow \equiv Si-O-\{M\} + 2\,(\equiv Si-\dot{O}) \ .$$

Bearing in mind that the number of vacancies in the atomic plane of a dislocation-free single crystal is approximately equal to the number of adatoms[108,243] and that the number of free-radical states of the type $\equiv \dot{S}i$ generated in the organosiloxane matrix is approximately equal to the number of states of the type $\equiv Si-O^{\cdot}$, the overall annihilation process in the interaction of free-radical states of the amorphous organosiloxane matrix and surface states of the type of the point defects of the silicon single crystal can be described by the equation[108]

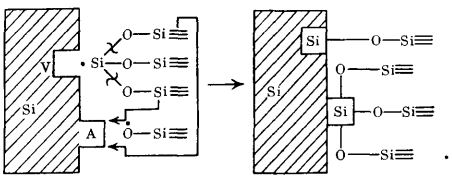
$$\equiv \dot{S}i + V\{M\}A + \dot{O}-Si\equiv \rightarrow \equiv Si-O-\{M\}-Si\equiv \qquad (4)$$

However, since the Si–Si bond formed as a result of reactions (3) and (4) in the systems considered (especially under the conditions of the saturation of the surface layers of the silicon single crystal with oxygen) is energetically unfavourable, it either dissociates or is oxidised further to form a siloxane linkage.

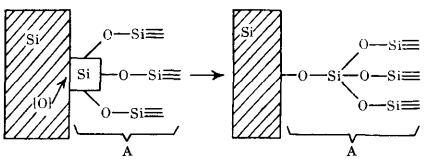
The mechanisms examined together with the processes involving the dislodging of the impurities sorbed on the surface of the natural oxide[54,169] and their sorption by the

amorphous phase of the dielectric can explain the decrease of the concentration of the surface states of single crystal silicon when it is protected by a POSSO film[108-111].

On the basis of the data of Andrianov et al.[108], the following mechanism for the interaction of a single silicon crystal with POSSO has been put forward[110,111]:



Taking into account data[239] for the atomic state of oxygen in the surface layer of a silicon single crystal, this mechanism can be refined:



with an increase of the functionality of the local cluster A from 3.0 to 3.25.

The results of a study of the photothermostimulated exoelectron emission over a wide temeprature range[120] may serve as confirmation of the mechanisms of the observed decrease of the concentration of interphase states. The experimental data obtained for systems comprising a POSSO film both on normal silicon and silicon of the *n*- and *p*-types lead to the important conclusion that there are two stages in the interaction. The first stage begins at the melting point of the oligomer and terminates with its complete conversion into the polymer. It is characterised by the fixation of the surface structures and the formation of an interface and in essence constitutes a pseudoepitaxial process in which an interfacial layer is formed on an ideal single crystal surface which continues on further increase of the ideality of the surface. This is manifested by a relative independence of the intensity of the exoelectron emission of temperature on the luminescence curves. The interaction between the film and the support decreases the regularity of the POSSO structure compared with the initial material as a consequence of the interaction with the layer of the natural oxide and the dissolution of the impurities sorbed by the natural oxide on the surface of the single crystal in the OOSSO melt with their subsequent sorption in the bulk of the infusible polymer[169,170] via the mechanisms presented above.

The temperature of the onset of the second stage of the interaction of the finished polymer with the support depends greatly on the defectiveness of the surface and the character of the impurities in the bulk of the silicon. For normal silicon, this temperature is in the range 377–393 °C and diminishes with increase of the concentration of the surface point defects. The structure of the spectrum of the photothermostimulated exoemission is in this case fairly simple and is characterised by a single broad luminescence band. Two emission maxima are observed for *n*-type silicon in the range 347–377 °C with a separation $\Delta T = 18$ °C and for *p*-type silicon there are two maxima in the range 393–423 °C with a separation $\Delta T = 7$ °C. This result can be explained by the different effects of the donor and acceptor impurities on the charge state of the surface point defects and the surface as a whole and is due to the different efficiencies of the annihilation of ionic and free-radical states of the type $\equiv Si^{O}$ and $\equiv \dot{S}i-O^{O}$, on the one hand, and $\equiv Si$ and $\equiv Si-O$, on the other.

The mechanism of the interaction of oligo- and poly-organosilasesquioxanes with single crystal silicon described[100,111,140,169,170] is useful in the development of a technology for polymerisation-filled composites, with dielectric characteristics modifiable within wide limits, on the basis of POSSO and transition metal oxides such as titanium dioxide or tin dioxide. In this case the filler particles can be regarded as single crystals. The activation of the filler surface makes it possible to increase the concentration of the active functional groups and to obtain a polymerisation-filled POSSO composite with 70 wt.% of tin dioxide as the filler bound to the polymer matrix via Si–O–Sn linkages.

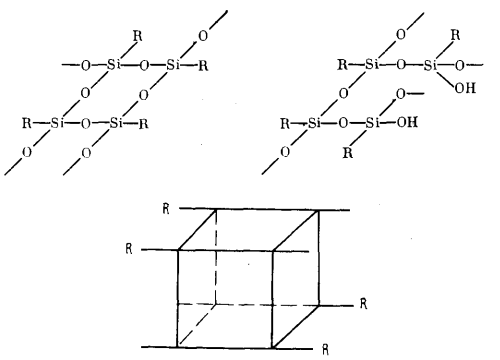
VI. THE STRUCTURE OF CYCLIC ORGANOSILASESQUIOXANES, OLIGO-ORGANOSILASESQUIOXANES, and POLY-ORGANOSILASESQUIOXANES

The discovery of the relation between the molecular structure and macroscopic characteristics of polymeric dielectrics[89,149,152] has stimulated studies on the molecular structure of POSSO and modified materials based on them. However, their electrical strength[244] and other electrophysical parameters depend greatly also on the character of the disorder of the condensed phase, which is analysed either in terms of the radial distribution function for monatomic materials (its application to a diatomic material[245] can lead to inaccuracies) or in terms of the atomic pair function[246]. The degree and character of the possible ordering in disordered tetrahedral structures, which are of definite interest for comparison with siloxane matrices, have been examined in two investigations[18,247].

Polyorganosiloxanes are tetra-atomic systems and accurate quantitative X-ray diffraction methods for the analysis of amorphous solids are inapplicable to their investigation. However, a number of studies have been carried out in order to obtain X-ray diffraction data to determine the most general characteristics such as the average interchain distances[82,116,124,248-250].

1. The Molecular Structure of Oligo- and Poly-organosilasequioxanes. The Statistical Copolymer Model

In order to reach a conclusion about the supermolecular organisation of a condensed non-ordered phase when limited structural data are available, it is necessary to have data on the molecular structure. The molecular structures of oligo- and poly-organosilasesquioxanes have been investigated[89] by infrared spectroscopy and NMR for a series of specimens with different functionalities obtained under different rigorously controlled conditions. The reaction products consisted of a complex mixture of oligomers whose MWD was determined by the process conditions. In addition, a study was made of the products of the thermal polycondensation of the oligomers obtained, of the high-temperature annealing of the polymers in air at 700 °C, and, for comparison, of amorphous silicon dioxide. The results of the infrared spectroscopic investigation of the specimens (Fig.9)[89,109-111,120] show that the structure of the molecules of oligo- and poly-organosiloxanes can include both planar and large three-dimensional cyclic units predominantly of the T_8 type.



The molecules of oligomers can incorporate all three types of cyclic units. The absorption band in the range 915–930 cm^{-1}, whose intensity decreases with decrease of the content of hydroxy-groups and can be assigned, according to Andrianov et al.[89], to the deformation vibrations of the OH group in a planar ring, in agreement with other data[251], is of definite interest.

Low-resolution NMR spectra[89] also indicate the absence of both intermolecular and intramolecular hydrogen bonds from the test specimens. The predominantly dispersion character of the intermolecular interaction is indicated, apart from the low mechanical characteristics, also by X-ray diffractometer data. All the oligo- and poly-organosiloxane specimens investigated are amorphous to X-rays regardless of the method of their preparation and the heat treatment conditions[89,110,111,120]. The maximum of the first amorphous halo occurs at 8.4 Å for oligomethylsilasesquioxanes regardless of their functionality $F = 3.0–3.25$; for oligophenylsilasesquioxanes, the maximum is at 12.8 Å, which agrees well with the value ~13 Å quoted in other studies[104,250], etc.

The data enumerated permit certain conclusions about the molecular structure of oligo- and poly-organosilasesquioxanes[89,109–111,120,140]. The structure can be described statistically by an average model incorporating structures of the T_8 type, in completely closed T_8 rings, closed and open rings of the type T_6 and T_4, and also statistically distributed OH groups. Here it is necessary to take into account the possibility of the involvement of fragments of smaller rings in the formation of the structures of larger rings. This model corresponds to the arrangement of the macromolecule in the form of a large helix[140] in which there are breaks in the rings ensuring the relaxation of structural stresses and segmentation at intervals corresponding to approximately one turn of the helix, which is consistent with the measured dimensions of the Kuhn segment[116]. If the analogy between OOSSO and POSSO, on the one hand, and silicates with large cations, on the other, is extended, one can postulate that the polyphenylsilasesquioxanes obtained under the conditions of the studies of Janin and Guyot[99] and Andrianov et al.[78] should resemble the xonotlite ribbon-like structures having unsatisfactory dielectric properties, while the OOSSO obtained under the conditions of the studies of Kamaritskii et al.[88] and Andrianov et al.[89] resemble more closely chrysotile asbestos or, what is even more likely, potassium cerium silicate with a three-dimensional anionic skeleton, namely $K_2CeSi_6O_{15}$,[252,253] whose structure constitutes a new example of an anionic purely silicon–oxygen skeleton made up of xonotlite ribbons which extend along the y axis and undergo a significant deformation due to the puckering of the rings and their mutual rotation in the xy plane. Direct condensation of the strips at the $z = 0$ and $z = 1/2$ levels leads to an open network of centrosymmetric eight-membered (xonotlite) rings and six-membered (lovozerite) rings perpendicular to them. When the rings are joined together, helices made up of tetrahedra around parallel z axes 2_1 arise. The formula of the skeletal anion does not have the standard form $[SiO_2]_{\infty\infty\infty}$ and is in fact $[Si_2O_5]_{\infty\infty\infty}$ owing to the presence of a single free O atom in each tetrahedron. In the formula of this silicate with eight-membered rings there are only six Si atoms, because the initial pair of atoms in the second ring constitutes the final pair of the first ring.

On the basis of the results of a number of investigations[78,79,88,89,104,110–113,120,128,140], we proposed a statistical copolymer model for OOSSO and POSSO, for both cyclic three-dimensional cage-like organosilasesquioxanes and for the compounds with the ladder structure. In the study of ladder POSSO, it was observed[78] that, on formation of ladder macromolecules with a double stranded cyclolinear structure, one of the essential stages involves the rearrangement of the cyclic three-dimensional ("cage-like") fragments. It has been pointed out that polyphenylsilasesquioxanes have a high degree of order only in individual polycyclic sections distributed statistically along the chain. Furthermore, it has been stated directly[104] that the elementary units of the macromolecular chain are polydisperse as regards dimensions. The fact that in the hydrolytic cocondensation of trichlorophenylsilane and trichlorovinylsilane in their mixture there are no products of their separate hydrolysis, mentioned above, is also striking[79].

2. The Study of the Phase Structure of Cyclo-, Oligo-, and Poly-organosiloxanes. The Interrelation of the Structural Forms

As stated above, the non-crystallisability of POSSO, noted in a number of studies[56,88,89,109–112,120,140,165], limits the applicability of diffraction methods also in the study of their structures[89]. The non-crystallisability of POSSO is determined to some extent by the skeletal structure of their molecules, because the possibility of a three-dimensional rearrangement of molecular fragments, requiring the dissociation of at least two of the three siloxane linkages, is virtually ruled out. The crystallisation of the synthetic material obtained by the thermal oxidation of POSSO, which inherits the molecular structure of the latter and whose composition $\{SiO_2\}_n$ is identical with that of silicon dioxide, requires the dissociation of $3n$ Si–O bonds[111].

A genetic approach to the morphological changes in siloxanes has been proposed[112], starting with the simplest rings [tetraphenyltetrahydroxycyclotetrasiloxane (T_4), its dimer hexaphenyltetrahydroxybicyclotetrasiloxane $(T_4)_2$, and octaphenylcyclo-octasilasesquioxane[159] (T_8)] and proceeding via the corresponding oligomers and pre-polymers to give infusible and insoluble polyphenylsilasesquioxanes. The compounds T_4 and T_8 are crystalline substances and X-ray diffraction data have been obtained for them by a standard diffractometric method using Cu K_α radiation and have been checked by an especially developed photomethod[254].

According to Andrianov et al.[89], neither oxidation-reduction nor disproportionation processes take place during the hydrolytic condensation of OCS. In the products of the hydrolytic condensation of OCS each silicon atom is linked to three oxygen atoms and to one organic group. Furthermore, it was shown in the same study[89] that the large molecules have a cyclic three-dimensional structure and consist mainly of alternating large (T_8) and small (T_4) rings. It follows from this that the problem of the description of the structure of oligo- and polyorganosilasesquioxanes can be reduced to a quantitative analysis of the contents of the above structural fragments.

A method based on the Selyakov–Scherrer spreading of the polycrystalline reflections of the T_4 and T_8 rings and on a graphical comparison of the curves thus obtained with the experimental curves for oligomers and polymers with different degrees of condensation has been proposed[112]. This procedure is carried out taking into account the influence of termination, in terms of the scattering angles allowed for, on the amorphous halo patterns[255]. The characteristics of the variation of the structural forms between two probable structural elements can be readily traced from the change in the positions of the first amorphous haloes of the oligomeric and polymeric materials; on the basis of these data, a nomogram has been constructed[112] for the quantitative analysis of the contents of the T_4 and T_8 structural fragments in macromolecules. This approach can be used also in the study of other polymers[256].

The presence of cyclic structures in amorphous polyorganosiloxanes makes it possible to discuss the results for crystalline cyclic organosilicon compounds[159,257–262]. X-Ray diffraction studies on the large rings of organosilasesquioxanes have been carried out[159–200,263–265]. In order to establish a relation between the non-equivalence of the silicon atoms and the distortion of the silicon–oxygen skeletons in ethyl- and vinyl-octacyclo-octasilasesquioxanes and to refine the structure of T_8, they were investigated by high-resolution NMR in the solid state[266]. The study of the infrared spectra[267], mass spectra[268], and volatility[269] made it possible to revise their molecular structures and to permit the development of a technology for their application. A study[143] involving the measurement of the vapour pressures of a series of OOSSO is also of interest in this sense.

VII. THE ADHESION CHARACTERISTICS OF LAYERS AND COATINGS BASED ON POLYORGANOSILASESQUIOXANES

The physicomechnical properties of POSSO have been examined in a number of studies[194,198,211,212,270]. One of the most important properties of a coating must be its effective adhesion to the support. It is known that adhesion depends on a multiplicity of factors and is determined by the properties of both the adhering substance and the substrate. A study has been made[212] of the dependence of the adhesion strength of a layer of POSSO on various supports on the chemical structure and the technology of the preparation of the film and of the adhesion properties of coatings based on polymethyl-, polyvinyl-, polymethylvinyl-, polymethylphenyl-, and polydichlorophenylmethyl-silasesquioxanes, obtained from solutions of the corresponding oligomers at different concentrations in the range 10–25 wt.% in solution in the 1:1 acetone–toluene mixture, which made it possible to obtain films of different thickness (ranging from 1.0 to 6.0 μm). A polished steel support proved to be most suitable for tests on adhesion strength. At the same time measurements were made of the dielectric characteristics of the material. At a concentration of the oligomer solution below 10 wt.%, there was almost no adhesion between the plates, which can apparently be explained by the impossibility of the formation of a monolithic film between them.

The adhesion strength of various POSSO in relation to a steel support increases, other conditions being equal, with increase of the oligomer concentration, reaching a limiting value at an OOSSO concentration of 20 wt.% and then remaining almost unchanged. The degree of adhesion depends strongly on the nature of the organic substituents at the silicon atoms and also on the conditions in the heat treatment of the specimens.

The adhesion strength of POSSO is definitely influenced by their functionality. The increase of the overall rigidity of the polymer film with increase of the functionality from 2.9 to 3.0 impairs the adhesion strength. This effect can be associated with the increase of the contribution of the relaxation phenomena with increase in elasticity and also with the change in the number of effective contacts at the adherent–substrate boundary.

There is a correlation between the adhesion strength and the angle of wetting of various supports by solutions of the corresponding OOSSO. It has been established[212] that oligophenylsilasesquioxanes are characterised by increasing wetting angles on various supports and that an increase of concentration entails an increase of the wetting angle. These features are common to a series of surfaces: steel, chromium-plated steel, single crystal silicon, glass, and gold-plated sital. Furthermore, it is known that the wettability of a surface improves (the wetting angle diminishes) with improvement of the quality of the preparation of the surface—a polished surface is wetted more effectively than a non-polished surface.

In the study of adhesion properties in a support–POSSO system account must be taken of a series of factors. The surfaces of the majority of supports are coated by a more or less thin layer of oxide and in these cases the properties of the surface hydroxy-groups are determined to a decisive extent by the nature and structure of these oxides[241]. The presence of reactive hydroxy-groups in OOSSO improves the adhesion of the dielectric coating to the supports. In this case, if the hydroxy-groups on the surface of the support are reactive with respect to the silanol bonds of the oligomer, condensation and grafting of the molecules to the surface take place. On the other hand, if the surface layer consists of adsorption water, there is a possibility of interaction with the rings, leading to the rupture of the surface layer of the oxide and then to direct interaction of the organosiloxane with the support, as happens in the aluminium–amorphous SiO_2 system[271].

The modification of POSSO both at the molecular level (for example, by introducing the aluminium heteroatom directly into the siloxane chain[128]) and in the bulk phase level exerts a major influence on the adhesion properties of such systems. However, one must then bear in mind that the bulk-phase modification usually leads to an appreciable impairment of the overall dielectric characteristics of the materials.

VIII. ELECTROPHYSICAL PROPERTIES OF POLYORGANOSILASESQUIOXANES AND MODIFIED MATERIALS BASED ON POLYORGANOSILOXANES

All the preceding discussion of both the synthesis and the technology of the preparation of oligo- and poly-organosilasesquioxanes and modified materials based on polyorganosiloxanes as well as their structure and physicomechanical characteristics was based on a single postulate, namely that the ultimate result must be the creation of materials with specified electrophysical, namely dielectric, properties: at the same time their compatibility with both traditional semiconductors[108–111] and with special purpose semiconductors, particularly organic semiconductors[1] as well as adequate advantages in the technology of electronic instrument making must be ensured. We shall consider the two most important methods for the investigation of the electrophysical properties of dielectrics—dielectric spectroscopy and polarisability of polyorganosilasesquioxanes and related materials,

the discussion being preceded by certain new ideas concerning the mechanism of the transport of current carriers in disordered dielectrics[272].

1. The Tunnel Electrical Conductivity of Disordered Dielectrics

In amorphous materials the lack of structural order induces the localisation of electronic states and determines the character of the conductivity of disordered polymeric dielectrics[272]. Electron transfer via localised states is described by methods of the permeation theory[273], which can be explained by a simplified model. The quantum nature of the jump conductivity permits the hypothesis of electron tunnelling between localised states. An attempt has been made[272] to develop a tunnel model of the electrical conductivity of disordered systems and to test it experimentally on amorphous polymeric dielectrics.

The analogous character of the calculated and experimental relations between the conductivity and the concentration of localisation centres confirms the validity of the model involving electron transfer via localised centres in polymeric disordered dielectrics[274].

The tunnel model proposed[272,274] leads to an expression for the electrical conductivity which agrees with the results of the permeation theory[273]. This model makes it possible to explain the deviations of the experimental results from calculations based on the permeation theory. It can be used to describe the electrical conductivity of disordered polymeric dielectrics.

2. Dielectric Spectroscopy of Polyorganosilasesquioxanes and Modified Materials based on Polyorganosiloxane

The quality of a dielectric material should be assessed and the scope and regions of its applications should be determined not so much in terms of each of the parameters enumerated at the beginning of the present study as, firstly, in terms of the sum of the dielectric properties (naturally subject to the condition that none of the parameters determining the usefulness of the material is below the lower limit), secondly, in terms of the possibility of altering within the required limits one or several parameters in accordance with the functional purpose of the material without a significant impairment of the sum of its dielectric properties, and, thirdly, in terms of the stability of both functionally significant parameters and the sum of the dielectric properties in relation to external influences[110,111], usually the influence of temperature or moisture content or their combined influence. The influences of radiation, gaseous atmospheres[56], acids, salts, bases[128], etc. must be regarded as other external influences of practical importance but encountered more rarely.

The dielectric parameters of PMSSO differ little from the characteristics of amorphous SiO_2. However, it has been shown[88] that, when the hydrolytic condensation of TCMS is carried out under otherwise optimal conditions, the values of tan δ and ε at different frequencies depend on the temperature of the synthesis. The knowledge of these relations makes it possible to obtain materials with specified characteristics and the modification is carried out using the differences in the course of the polycondensations of oligomers at different temperatures[275]. The dielectric properties can be altered by this procedure only within certain limits.

Significantly greater changes in the parameters of the substance can be achieved by chemical doping (or by the introduction of a heteroatom) directly into the siloxane chain[120,211], or by employing a molecular fragment whose chemical nature is different from that of the organosiloxane matrix[194], or by the structural modification of polyorganosiloxanes. Better results can be achieved by the last method than by chemical doping, but, within fairly narrow limits of the modifier concentrations, all the relations governing the properties of the material (both electrophysical and physicochemical) pass through a sharp maximum with increase of the concentration of the dopant owing to the appearance of the heterophase of the modifier or its reaction products. Although the introduction of a heteroatom into the siloxane chain causes a smaller change in the dielectric characteristics, it leads to the precipitation of the heterophase and ensures a high resistance to external influences, since the modification is carried out at the molecular level.

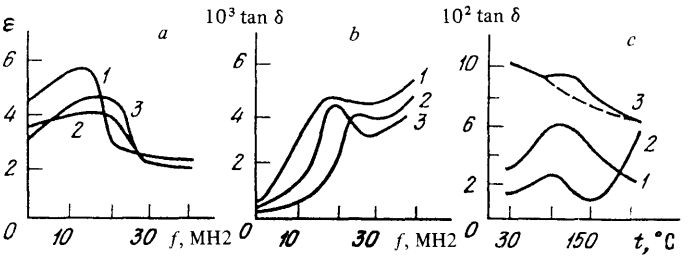


Figure 10. Dielectric spectroscopy of polyorganoaluminosiloxanes: *a*) frequency dependence of the dielectric constant ε; *b*) frequency dependence of the tangent of the dielectric loss angle tan δ; *a* and *b*: 1) MM-12; 2) MV-12; 3) MF-13.2; *c*) temperature dependence of tan δ for MM-12 at different frequencies (Hz): 1) 5×10^4; 2) 2×10^6; 3) 4×10^6.[128]

The dielectric parameters (ε and tan δ) of films based on polyorganoaluminosiloxanes have been investigated[128] over a wide range of frequencies and temperatures (Fig.10). Calculation of the relaxation time from the frequency of the maximum of the dielectric losses (Fig.10*b*) yields $(6-8) \times 10^{-9}$ s, which is characteristic of dipoles or dipolar complexes with a high molecular weight. The temperature variation of tan δ (Fig.10*c*) has a characteristic dielectric losses maximum at a temperature which is higher the higher the frequency, while ε initially increases with temperature, which can be accounted for by the increase of the mobility of the fragments of the polymer molecules resulting in a facilitation of the orientation of the dipoles. On further increase of temperature, the intensification of thermal vibrations reduces the degree of order and ε falls after it has passed through a maximum. Films based on polyorganoaluminosiloxanes have fairly low values of tan δ over a wide temperature range up to 350–400 °C, which makes it possible to classify them as high-temperature dielectrics. At low frequencies the values of ε and tan δ diminish with increase of the aluminium content in the siloxane chain, which is apparently associated with the increase of the rigidity of the polymer structure, while at high frequencies, where polyaluminosiloxanes can be regarded as non-polar dielectrics, ε and tan δ are almost independent of the aluminium content in the polymer. The electrical strength of such films increases slightly with increasing aluminium content in the siloxane matrix.

3. The Polarisability of Modified Polyorganosiloxanes. The Electret Effect

The polarisability of dielectrics is one of their fundamental characteristics which makes it possible to discover the kinetic relations governing the accumulation and dissipation of the charge. All the effects occurring on active dielectrics—the charge bond, the electret effect, and others—are determined, when other dielectric properties are satisfactory, by their polarisability.

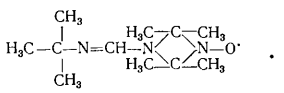
The results of studies of the processes involving the accumulation and dissipation of charges in electrets for various methods of imparting an electric charge (thermo-, electro-, and tribo-electrets) and studies of the influence of a large number of external stabilising and destabilising factors (acoustic, thermal, electromagnetic, and combined influences) have been described[123]. It was established that, when electrets, including PMSSO, are subjected to an acoustic influence, the spectrum of the relaxation times of the charges changes and the relaxation times τ diminish to a greater extent the more prolonged the influence. It has been noted that electrets with a higher level of charge (>100 V) are less stable when subjected to an acoustic influence of long duration. Comparison of different influences leads to the following relation between the relaxation times:

$$\tau(\text{control}) \gg \tau(\text{acoustic}) \gtrsim \tau(\text{electromagnetic}) > \tau(\text{combined}).$$

In a polarised dielectric medium the phase velocity V_ϕ of ultrasound increases with increase of the space density of the electric charge Q_V. For example, in poly(methyl methacrylate) a change in Q_V by 1×10^2 C m^{-3} alters V_α by 10%.[193]

The characteristic features of the electret effect are investigated by studying the spectrum of the electric states of localised charge carriers in polarised dielectrics. Specific modification of the capture centres by the introduction of donor–acceptor additives[165,211] into the polymer matrix alters the spectrum of the charge relaxation times of the electret and the differentiation of additional TSD current peaks makes it possible to relate models of the capture centres to the structure of the polymer at the molecular level[276].

Thus the kinetic characteristics of electrets based on PMSSO and modified materials obtained by the chemical polycondensation of OMSSO and an oligomer in the presence of an electron-donating additive in the form of a long-lived free radical R have been studied[165]:



The concentration of this radical is 0–10 wt.%. A discrete measurement of the electret potential difference $U_k(t)$ was carried out. In order to compare the characteristics of electrets with different initial potential differences $U_k(0)$, the time variation of the dimensionless quantity $k = U_k(t)/(U_k(0)$ was analysed. The OMSSO polycondensation phenomena and the structural changes in the specimens on polycondensation were investigated by gravimetric, X-ray diffraction, and EPR methods. In the course of the increase of the polarisation potential U_n from 0.5 to 4.0 kV, a change in the sign of $U_k(0)$ as a consequence of the reverse discharge effect was observed. The study of the structural changes in the oligomer following the introduction of R demonstrated an increase of the average interatomic distances r and Δr and a redistribution of the contributions of the scattered intensity owing to the increase of the contribution of scattering by atoms and the decrease of the contribution of scattering by chains. The magnitude of the effect is proportional to the concentration of the radicals R. During polarisation, the influence of the injected radicals R passes through a minimum[165] because they are involved in at least two competing reactions—chain termination and the grafting of the radical to the groups around the siloxane chain. The latter reaction determines the polarisation of the polymer and the generation of a stable electret state.

IX. CONCLUSION

The wide range of applications of highly functional organosilicon polymers[42,46,49–54,56,57,75,98,107–111,120,128,151,152,165,190,193,208,215,217,234,277] can be supplemented by applications in which their dielectric properties play an important but not a decisive role and the entire set of the useful properties of materials based on them is employed[194,278,279]. Clearly such polymers have a whole series of other useful qualities, among which one may mention thermal, plasma, and tracking stability, but evidently their joint survey within the framework of a single article is impossible.

The methods developed for the conversion of soluble and fusible oligomers[49,56,57,75,88,104,108–111,120,128,140,165,169,170,211,212,275] lead to the formation of polymers with the required properties only when oligomers with rigorously defined properties are used as the starting materials and with a rigorous maintenance of specific conditions in the polycondensation process. The presence in the oligomer of even filterable gel particles results in a sharp impairment of the dielectric characteristics of materials based on POSSO. Highly functional oligomers are metastable and, depending on the degree of purification and the storage conditions, their properties deteriorate more or less rapidly and they give rise to products with a wider range of MWD, up to the formation of gel particles.

One of the most important stages in the technological chain leading to the preparation of the materials is therefore the first stage in which soluble and fusible oligomers with a specific set of physicochemical characteristics (average molecular weight, MWD, the number of hydroxy-groups, the content of limiting impurities, etc.) are formed[89,92,93]. The formation of such oligomers requires an appropriate organisation of the technological process. The chemical nature of the hardening processes and of the interaction with the supports is also determined by the technological conditions. Thus the formation of materials based on metastable substances is determined at the technological level.

The dependence of the dielectric properties of materials on the molecular and phase structure of the polymer, on the one hand, and the distinct dependence of its structure on the synthesis conditions, on the other[70,88], show that the quality of the polymeric materials is in many respects determined by the methods, technological procedures, and the conditions in the preparation of oligomers as well as the monitoring of the intermediate products, since the parameters of the future material and the quality of the articles made from it are in fact determined at this level.

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The Electret Effect in Polymers. Advances in the Preparation and Application of Electrets

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Recent advances in the development of the theory of electret effects in polymers (except photo- and bio-electrets) are discussed: they include the phenomenological theory, the nature of the residual polarisation and of the injected charge, and the nature of the piezo- and pyro-effects in polymer electrets. Successful applications of electret-thermal analysis to the study of molecular mobility in polymers are discussed. The principal directions of the practical exploitation of polymer electrets are outlined. The goals of further studies and of technological developments are defined. 99 references.

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I. INTRODUCTION

The term electret effect describes the ability of dielectrics to develop electric charges and retain them for long times. Polymer electrets can be prepared by various methods: by cooling the polymer in an electric field (thermo-electrets), by polymerisation or cross-linking in an electric field (chemo-electrets), by the application of a strong electric field (electro-electrets), by charging in a corona discharge (corona electrets), by exposure to radiation (e.g. to an electron beam, radiation electrets), and by evaporating a solution of the polymer in an electric field (cryo-electrets). Electrets have been obtained also by mechanical deformation (mechano-electrets), by frictional electrification (tribo-electrets), and by exposing a polymer to a magnetic field (magneto-electrets).[1]

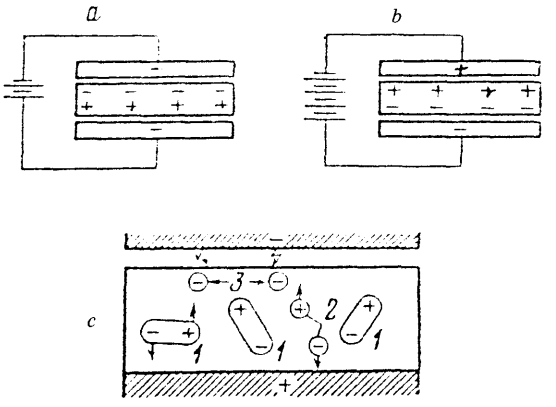


Figure 1. Configuration of charge and electrodes in an electret: (*a*) hetero-charged electret, (*b*) homo-charged electret, (*c*) charges in the electret (*1*, oriented dipole, and dipoles undergoing orientation; *2*, displaced ions; *3*, injected charge carriers).

Electrets can be classified according to the type of charge into those whose charge is due to the orientation of dipoles and the displacement of ions "frozen" in the electric field, and which therefore retain a residual polarisation P or "hetero-charge", and the electrets whose charge is due to carriers injected from outside ("homo-charge", or real free charge σ_p, see Fig.1). In a real electret the surface charge density σ_{eff} is equal to the sum of these two types of charge (of opposite sign):

$$\sigma_{eff}=\sigma_p-P\,.$$

If residual polarisation is initially absent ($P = 0$), some polarisation will appear during storage under the influence of the internal field of the electret. The changes in surface charge density are determined by the time dependence of σ_p and P.

II. FORMATION AND STABILITY OF ELECTRET CHARGES

1. Phenomenological Theory

The phenomenological theory of electrets gives a general description of the electret effect. By formulating various hypotheses on the role of the charges σ_p and P different expressions can be obtained for the time dependence $\sigma_{eff}(t)$. A detailed phenomenological theory was developed by Gubkin[2], who also discussed alternative phenomenological theories.

According to modern views, electrets contain a residual, frozen polarisation P and a real charge σ_p. It is usually assumed that the polarisation decays by an exponential law with a relaxation time τ_p, and that the real charge also decreases exponentially and is determined by the Maxwell relaxation time τ_M:

$$\begin{gathered}P(t)=P_0\exp(-t/\tau_p)\\ \sigma_p(t)=\sigma_p(0)\exp(-t/\tau_M)\\ \tau_M=\varepsilon_0\varepsilon\rho\,.\end{gathered}\qquad(1)$$

In these expressions P_0 and $\sigma_p(0)$ are the initial values of P and σ_p, ρ is the (volume) electrical resistivity, ε is the dielectric constant, and ε_0 is the permittivity of free space 8.854×10^{-12} F m^{-1}. If electrodes are placed near the electret, and a gap l is left between the electret surface and the electrodes, the parameter ε in Eqn.(1) is replaced by the coefficient K, defined as

$$K=\varepsilon+L/l$$

where L is the thickness of the electret[2]. The result is an expression in the form of

$$\frac{d\sigma_{eff}(t)}{dt} + \frac{\sigma_{eff}(t)}{\varepsilon_0 K\rho} + \frac{dP(t)}{dt} = 0 .$$

In the theory developed by Perlman[3] no allowance is made for the formation of residual polarisation during the preparation of the electret: a "ready-made" electro-electret is assumed, and only the changes in polarisation due to ageing are discussed. Other workers used slightly different initial assumptions[4,5], but they all obtained expressions of the type of

$$\sigma_{eff}(t) = \sum_i \sigma_i(0) \exp(-t/\tau_i)$$

where in most cases $i = 1, 2, 3$.

Let us consider the case of the thermo-electret. The expression for the polarisation induced by the internal field of the electret during ageing is

$$P = \varepsilon_0 \int_0^t E(t') \frac{d\chi(t-t')}{dt'} dt$$

where E is the intensity of the internal field of the electret, χ is the dielectric susceptibility, consisting of the susceptibility corresponding to polarisation, $\chi_\infty = (\varepsilon - 1)$, established instantaneously and constant in time, and the time-dependent susceptibility $\chi_p(t)$, associated with the polarisation slowly induced under the influence of the internal field:

$$P = P_{max}(1 - e^{-t/\tau_p})$$

where $P_{max} = P_0 = \varepsilon_0 \Delta\varepsilon E$ (and $\Delta\varepsilon$ is the increment of the dielectric constant, see below). The general time dependence $\sigma_{eff}(t)$ in this case becomes

$$\sigma_{eff}(t) = \sigma_p(0) e^{-t/\tau_M} - P_0 e^{-t/\tau_p} - \frac{1}{\varepsilon\varepsilon_0} \int_0^t \sigma_{eff}(t) \frac{d[\chi(t-t')]}{dt'} dt .$$

By solving this equation (using the Laplace transform) we obtain the following expression for an open-circuited electret

$$\sigma_{eff}(t) = \frac{\sigma_p(0)[(1/\tau_p) - (1/\tau_M)]}{[(1/\tau) - (1/\tau_M)]} e^{-t/\tau_M} + \left[\frac{\sigma_p(0)(\Delta\varepsilon/\varepsilon\tau_p)}{(1/\tau) - (1/\tau_M)} - P_0\right] e^{-t/\tau} \quad (2)$$

where $\tau = \tau_p \varepsilon/(\varepsilon + \Delta\varepsilon)$. Putting $\varepsilon = \varepsilon_\infty$ and $\Delta\varepsilon + \varepsilon_\infty = \varepsilon_{st}$ we obtain $\tau = \tau_p \varepsilon_\infty / \varepsilon_{st}$, i.e. an expression for the decay time constant of the charge, where τ_p is the rise time constant of the charge in the same condenser[6].

In real electrets τ_p is often much smaller than τ_M: in this case Eqn.(2) simplifies to

$$\sigma_{eff}(t) = \frac{\varepsilon\sigma_p(0)}{\varepsilon + \Delta\varepsilon} e^{-t/\tau_M} + \left[\sigma_p(0)\frac{\Delta\varepsilon}{\varepsilon + \Delta\varepsilon} - P_0\right] e^{-t/\tau} . \quad (3)$$

or

$$\sigma_{eff}(t) = \frac{\varepsilon_\infty}{\varepsilon_{st}} \sigma_p(0) e^{-t/\tau_M} + \left[\frac{\varepsilon_{ст} - \varepsilon_\infty}{\varepsilon_{st}} \sigma_p(0) - P_0\right] e^{-t/\tau} . \quad (4)$$

In the presence of a gap between the electrode and the electret we replace ε by K in Eqns.(3) and (4).

In practice the real charge is often found to have two components: a rapidly decaying (σ'_p) and a slowly decaying (σ_p) component. Assuming that the decay time constant of σ'_p is so small that slow polarisation cannot develop in the field of this charge we obtain

$$\sigma_{eff}(t) = \sigma'_p(0) e^{-t/\tau'_M} + \frac{\varepsilon_\infty}{\varepsilon_{st}} \sigma_p(0) e^{-t/\tau_M} + \left[\frac{\varepsilon_{st} - \varepsilon_\infty}{\varepsilon_{st}} \sigma_p(0) - P_0\right] e^{-t/\tau} . \quad (5)$$

Each term in Eqn.(5) has a clear physical significance. The first describes the capture of injected carriers by shallow traps near the surface of the dielectric. The σ'_p component of the charge plays an important role in static electrification and in charging in a corona discharge[7]: this charge can easily be removed by wrapping the electret in a metal foil or by applying an earthed electrode to it.

The second term depends on the capture of injected carriers by deep traps, whose energy is relatively high (see below). Thus the charge component σ_p can relax (at least partially) through compensation by the charge carriers of the polymer itself, and therefore the activation energy for the relaxation of this charge component at temperatures above the glass transition point is equal to the temperature coefficient of the conductivity of the polymer[8].

The third term in (5) is determined by polarisation. A thermo-electret prepared from a polar polymer will have a residual polarisation P_0. Since in many cases $\tau < \tau_M$ the presence of P_0 shortens the time needed to stabilise the electret. From the plots (Fig.2) of the $\sigma_{eff}(t)$ dependence for an electret charged in a corona discharge and for a thermo-electret we note that the latter stabilises relatively quickly whereas the former needs a long time to reach a quasi-constant value of σ_{eff}. [Stability is defined as a state in which σ_{eff} remains within a prescribed range (±15%, say) of its nominal value throughout the useful life of the electret (10 years, say).] Stabilisation can be accelerated by corona charging at elevated temperatures or by heating the already charged electret. In this case τ decreases, and a quasi-constant value of σ_{eff} is established more rapidly. For a polymer with a small value of the difference $\varepsilon_{st} - \varepsilon_\infty$ (i.e. a non-polar polymer), or a polymer with $\tau \geq \tau_M$ (a polar polymer with a very high glass transition temperature, such as a polycarbonate with a norbornane ring[9]) the stabilisation time is reduced to the very short time needed for the decay of the σ'_p component. We note that a good example of a non-polar polymer suitable for the preparation of stable electrets is a film of polytetrafluoroethylene or of the copolymer of tetrafluoroethylene and hexafluoropropene.

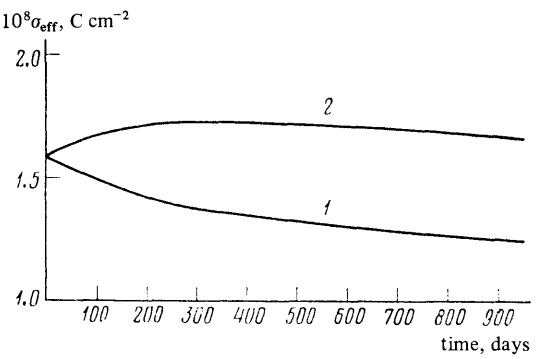


Figure 2. Time dependence of the surface charge σ_{eff} of electrets made from a polar polymer (polycarbonate): *1*) corona electret, *2*) thermo-electret ($\rho_{res} = 1.3 \times 10^{21}$ Ohm cm, $\varepsilon = 3$, $\Delta\varepsilon = 0.44$, $\tau = 8 \times 10^6$ s).

The constancy of P is determined by the molecular mobility, whereas the stability of the charge σ_p is determined by the electrical conductivity (which is also largely dependent, however, on the molecular mobility).

Polarisation can arise also in the crystalline regions of polar polymers. Thus, a rearrangement of the crystalline structure can be induced in poly(vinylidene fluoride) and polyamide-11 by strong electric fields [over 10^8 V m^{-1} in the case

of poly(vinylidene fluoride)]. Rotation of the $-CH_2-CF_2-$ chain in the direction of the field is energetically favourable, and results in a change of the crystal structure from the low-polarity α form to the more polar, spontaneously polarisable β form, in which P_0 can be as high as 0.1 C m^{-2}.[10]

2. Residual Polarisation

Let us consider the development of residual polarisation[11]. We shall heat the dielectric to the polarisation temperature T_p, which is higher than the transition temperature (for example, the glass transition temperature T_g, see Fig. 3). At temperature T_p the dielectric constant rises as a result of the increased segmental mobility which allows the dipoles to become oriented in the field. When the electric field E_p is applied the polarisation of the sample is described by the equation

$$P(T_p) = \varepsilon_0[\varepsilon(T_p) - 1] \cdot E_p \ .$$

If the dielectric is now cooled in the field to the temperature T_K, where $T_K < T_g$, and the external field is removed, the polarisation of the sample decreases by the amount

$$P(T_K) = \varepsilon_0[\varepsilon(T_K) - 1]E_p \ .$$

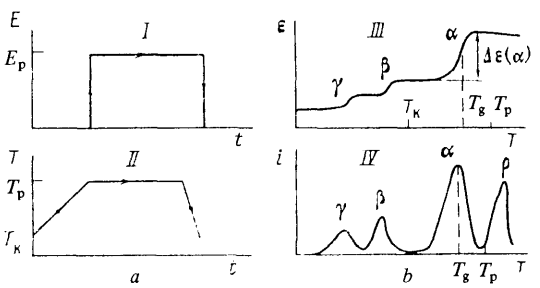


Figure 3. Preparation of a thermo-electret. (*a*) time dependences: *I*) field strength E_p, *II*) temperature *T*; (*b*) temperature dependences: *III*) dielectric constant, *IV*) TSD current during heating of the thermo-electret.

Since $\varepsilon(T_p)$ is greater than $\varepsilon(T_K)$, $P(T_p)$ is greater than $P(T_K)$, and the difference between these quantities is equal to the residual polarisation:

$$P_0 = P(T_p) - P(T_K) = \varepsilon_0[\varepsilon(T_p) - \varepsilon(T_K)]E_p \qquad (6)$$

or

$$P_0 = \varepsilon_0 \Delta\varepsilon E_p \ .$$

Here $\Delta\varepsilon$ is the temperature increment of the dielectric constant, approximately equal to the frequency increment of the dielectric constant at the transition temperature T_g: $\Delta\varepsilon \cong \varepsilon_{st} - \varepsilon_\infty$ (where ε_{st} is the static dielectric constant, and ε_∞ is the dielectric constant for a field of infinite frequency). Thus we have

$$P_0 = \varepsilon_0(\varepsilon_{st} - \varepsilon_\infty)E_p \ . \qquad (7)$$

The equality of P_0 [calculated by formula (6)] and of the heterocharge was established experimentally for polycarbonate and poly(methyl methacrylate) thermo-electrets polarised at $E_p < 10^6$ V m^{-1}, for which the injection of charge carriers is small. The values of $P(T_p)$ and $P(T_K)$ can be determined experimentally by integrating the charging currents at T_p and the discharge currents at T_K (after subtracting the conduction currents):

$$P(T_p) = \int_0^\infty i_p(T_p)\,dt; \quad P(T_K) = \int_0^\infty i_p(T_K)\,dt$$

where i_p is the current density.

However, the relationship (7) is not obeyed if we use the frequency increment of the dielectric constant obtained from the frequency dependence of ε′ and ε″ at temperatures higher than T_g.

It has been reported[12] that in polar polymers such as poly(vinyl chloride) the dielectric constant in the glass transition region increases as the measurement frequency is decreased to 0.1, 0.01, and 0.001 Hz, and the effect was ascribed to the increase in the effective dipole moment μ_{eff} caused by the increase in length of the segment (the mobile portion of the chain). Since $\Delta\varepsilon$ is proportional to $N\mu_{eff}^2$,

$$\Delta\varepsilon \simeq \text{const} \cdot N\mu_{eff}^2/T$$

an increase in the length of the segment (by a factor of 2, say) lowers the concentration *N* of dipoles by the same factor, but it raises μ_{eff}^2 by a factor of 4 (the parameter μ_{eff} contains contributions from all the groups present in the segment: $\mu_{eff} \cong n\mu_0$). The steep increase of ε near T_g is treated[12] as a typical ferroelectric effect, and T_g is identified with the Curie temperature of poly(vinyl chloride).

Thus Eqn. (7) is valid only if the measurement of ε is carried out under the conditions used in the preparation of the electret (frequency range, polarisation and depolarisation time, field strength). The dielectric losses ε″ and the dielectric constant ε′ can be calculated from the charging and discharging currents by using the Fourier transform

$$\varepsilon'' = \frac{1}{C_0 V}\int_0^\infty i_p \sin\omega t \cdot dt$$

$$\varepsilon' = \frac{1}{C_0 V}\int_0^\infty i_p \cos\omega t \cdot dt \ .$$

For ε″ we have the simplified formula[13]

$$\varepsilon'' = i_a/2\pi f_{equiv} C_0 V \ .$$

The equivalent frequency of the measurements is given by the expression

$$f_{equiv} = 0{,}1/t_p \ . \qquad (8)$$

Since the polarisation time t_p is tens of minutes, $f_{equiv} \cong 10^{-2}-10^{-4}$ Hz. Since electrets are stored for many months or years, the parameters ε and $\Delta\varepsilon$ which appear in expressions (2)–(5) should be determined at $f_{equiv} \cong 10^{-6}-10^{-9}$ Hz.

3. Charge Injection

The application of a strong electric field to a polymer causes injection of charge carriers into the polymer. The stability of this charge (σ_p) is formally determined by the electrical conductivity $\gamma = 1/\rho$. There are two different theories of the nature of electrical conduction in polymers. According to the first the electrical conductivity of polymers is ionic and depends on the concentration of impurities[14]. According to the second it is of the electron–hole type[15]. Ionic conduction is predominant at temperatures above T_g, when the segmental mobility is high, and also in plasticised polymers, for example of the poly(vinyl chloride) type.

Electronic charge transfer processes are predominant at high field strengths (above 10^6 V m^{-1}) in polymers at temperatures below T_g, in polymers with conjugated bonds (semiconducting polymers), and in polymer dielectrics with a relatively large number of conjugated bonds (for example, poly-imides[16]). However, even at low temperatures (below T_g) the contact charging of a dielectric without an applied external field on a clean surface in a vacuum takes place by electron transfer[17], whereas in air the charging is determined by the migration of ions in the adsorption layers on the surface[18].

The injected charge σ_p is produced by the injection of electrons and holes from the electrodes[19] (electro- and thermo-electrets), the injection of electrons, holes, and (or) ions from the air (corona electrets, electro- and thermo-electrets with a poor electrode–electret contact), the injection of electrons, holes, and ions from a liquid (in the case of charging from liquid electrodes), and by electron injection when the sample is irradiated with a beam of electrons. During charging in a corona discharge the main process consists in sorption of ionised air molecules on the polymer surface followed by electron transfer (from the molecule to the surface) and desorption of the molecules. At normal field strengths the charge carriers penetrate to a small depth into the polymer dielectric (1–1.5 μm), forming a charged layer ("cloud") which slowly diffuses into the dielectric[20]. The surface layer of dielectric with its high concentration of injected carriers has an abnormally high electrical conductivity. Depending on the "short-circuiting" conditions of the electret (i.e. on the disposition of the electrodes) the charge carriers will diffuse under the influence of the field of the electret either into the bulk of the sample or towards the nearest surface. When the electret is stored some of the carriers in shallow traps are captured by the deep traps. The depth of these traps determines the stability of the charge σ_p. The retrapping of the charge carriers can be accelerated by heating the electret.

The nature of the deep traps, which determines the value and the stability of σ_p, is discussed in Ref. 21. The injected charge carriers interact with the polymer molecules. For example, the interaction of electrons with a fluorinated polyolefin chain (polytetrafluoro-ethylene, tetrafluoro-ethylene–hexafluoro-propene copolymer) produces stable ions because of the high electron affinity of the fluorine molecule. The electrons can also interact with the carbonyl group to give charged groups of the $CH_2–CO^-–CH_2–$ type[22].

Impurity ions and phase separation boundaries can also act as traps. Electrons near an amorphous–crystalline interface of the polymer are slowed down, and their field induces the reorientation of neighbouring dipoles and polar groups. If the adjacent units of the molecular chain have sufficient mobility, the conformation of the chain can change. For example, in poly(ethylene terephthalate), studied by frustrated total internal reflection i.r. spectroscopy, charging in a corona discharge produces a change in the conformation of the chains in the surface layer: the *trans* conformation is partially converted into the *gauche* conformation according to the observed changes in the i.r. spectral absorption bands at 502, 633, 897, 973, and 1172 cm^{-1}. When the electret is discharged the original conformation is partially restored[23].

Studies of the thermally stimulated depolarisation currents of electrets containing injected charges have shown that the TSD maxima for the discharge of injected homo-charge (ρ maxima) occur at the same temperatures as the maxima of the molecular mobility at the crystallite boundaries (α_c relaxation). We should stress that this type of molecular mobility can seldom be detected by the traditional methods of dielectric spectroscopy because the contributing dipoles are weak and few in number: the position of the ρ maximum on the temperature scale corresponds to the maximum of the dynamic mechanical losses at a frequency of ~10^{-4} Hz.[24] Increasing the aggregate surface area of the crystallites per unit volume of the polymer (for example, by decreasing the crystallite size while keeping the overall crystallinity constant) raises the α_c maximum, i.e. it increases the trapped charge (for example, in polychlorotrifluoroethylene).[25]

The TSD current maximum corresponding to relaxation of the injected charge is called the ρ maximum because the activation energy for the relaxation of this component of the charge is equal to the temperature coefficient of the electrical resistivity ρ. Evidently, charge relaxation is due to the mobility of the polymer ions or of the injected ions: the motion of these ions can compensate the trapped space charge.

4. Surface Density of Charges

The time for which the surface density of charge σ_{eff} persists is determined by the stability of σ_p and P. Ultimately, the determining factor is the low electrical conductivity of the electret, which is produced in polymer dielectrics by a low concentration of intrinsic, free charge carriers and also (under the normal conditions of use of the electret) by a low internal field, especially if the electret is "shorted", i.e. in the presence of closely spaced electrodes. Under these conditions the electrical conductivity of the sample falls to 10^{-23} Ohm^{-1} m^{-1} or less[26].

The maximum value of the charge σ_{eff} is limited by the dielectric strength of air[1]. It increases as the thickness of the electret decreases:

$$\sigma_{eff}^{max} = 100\,\varepsilon_0[200 + (3\varepsilon/L)^{1/2}]^2 .$$

In this expression ε is the dielectric constant of the electret. On the other hand the maximum surface potential V_{max} decreases as the thickness decreases: $V = \sigma_{eff}L/\varepsilon\varepsilon_0$. For samples 2 mm thick the maximum value of σ_{eff} is ~5×10^{-5} C m^{-2}, and for films 10 μm thick it is ~2×10^{-4} C m^{-2}.[1]

III. THE ELECTRET EFFECT IN POLYMERS

1. Electret-thermal Analysis of Polymers

The study of the kinetic relaxation characteristics of electret charges can be greater accelerated by a programmed heating of the electret with measurement of the thermally stimulated depolarisation (TSD) current.

The relaxation parameters are calculated from the TSD currents[11] by formulae which assume that 1) the electret contains only one type of dipole, 2) all the dipoles have the same relaxation time τ, and 3) the temperature dependence of the relaxation time is exponential,

$$\tau = A \exp(W/RT)$$

where R is the gas constant, A is the pre-exponential factor, and W is the activation energy (temperature coefficient) of the charge relaxation. With these assumptions we obtain the following formula for the TSD current of an electret heated at a linear rate b:[27–29]

$$i(T) = -\frac{P_0}{A}\exp\left[-\frac{W}{RT} - \frac{1}{bA}\int_{T_0}^{T}\exp\left(-\frac{W}{RT}\right)dT\right] \qquad (9)$$

where T_0 is the initial temperature. The relaxation time of the charge (τ_{max}) at the temperature of the TSD current maximum is given by the expression

$$\tau_{max} = RT^2_{max}/Wb\,. \qquad (10)$$

In the initial portion of the plot of TSD current against temperature we can use the expression

$$\lg i = \text{const} - 0{,}4343\ W/RT\,. \qquad (11)$$

By using Eqns.(9)–(11) we can calculate the macroscopic characteristics W, T_{max}, and A. However, these quantities cannot be related to the characteristics of the dielectric relaxation of the polymer obtained from measurements over a range of frequency and temperature. This is most probably because the above assumptions are never strictly applicable. Polymers often contain several types of dipole (polar groups), or if they contain dipoles of one type only their mobility can arise in two ways: either cooperatively, in a relatively long section (segment) of the macromolecule, or by being in a short side-chain (possibly in conjunction with other groups of the chain). The former alternative gives dielectric losses of the dipole segment type, the latter of the dipole group type. The second assumption (that all the dipoles have the same relaxation time) is also invalid. Polymers always show some range of dipole relaxation times, characterised by a distribution function. If the form of this function is known (for example, a Cole–Cole or a Fuoss–Kirkwood distribution) the expressions which relate the complex dielectric constant ε^* to the relaxation time become simpler, and the relationships of the components ε' and ε'' with each other and with the relaxation time are also simplified. The third assumption is exactly satisfied for dipole group relaxation and approximately satisfied for dipole segment relaxation.

These considerations suggest that the relaxation characteristics of the electret charges obtained from the TSD currents may be correlated with the characteristics normally used in dielectric spectroscopy. The charging current of a condenser in which the dielectric relaxation is described by the Cole–Cole theory is given by the formula[13]

$$i_p = \frac{Q}{\tau}\frac{1}{\Gamma(1-\alpha)}\left(\frac{t}{\tau}\right)^{1-\alpha} \text{(for } t \ll \tau)\,.$$

It follows from this expression that for a change in the temperature of the experiment (which results in a change of τ) we can write

$$i_p = \text{const}\cdot t^{-(1-\alpha)}\exp[-(1-\alpha)E/RT]\,.$$

Thus the experimental temperature coefficient W is related to the apparent activation energy of the dipole relaxation E by the expression

$$W = (1-\alpha)E \qquad (12)$$

where $(1 - \alpha)$ is a parameter which characterises the distribution of relaxation times according to the Cole–Cole theory, and is approximately equal to the distribution parameter λ of the Fuoss–Kirkwood theory[13]. By allowing for Eqn.(12) we can use formulae (9)–(11) to determine the dielectric relaxation parameters in the low frequency region if we also note that determining the relaxation characteristics from the TSD currents is equivalent to determining the dielectric losses at the frequency f_{equiv} by Eqn.(8) with $t_p = \tau_{max}$ [where τ_{max} is given by Eqn.(10)].

A more satisfactory description of the experimental results can be obtained by assuming that the parameters E and λ are independent of temperature[11]. In this case the TSD current is given by the expression

$$i(T) = -\frac{P_0 E\lambda b}{\pi RT^2}\,\text{sech}\left[\frac{E\lambda}{R}\left(\frac{1}{T}-\frac{1}{T_{max}}\right)\right] \qquad (13)$$

where T_{max} is the reference temperature, which for large values of E/RT becomes equal to the temperature of the TSD current peak.

The dielectric losses at the frequency f_{equiv} can be calculated if the TSD current is known:

$$\varepsilon''(T) = \pi RT^2 i(T)/2\varepsilon_0 E E_p b\,. \qquad (14)$$

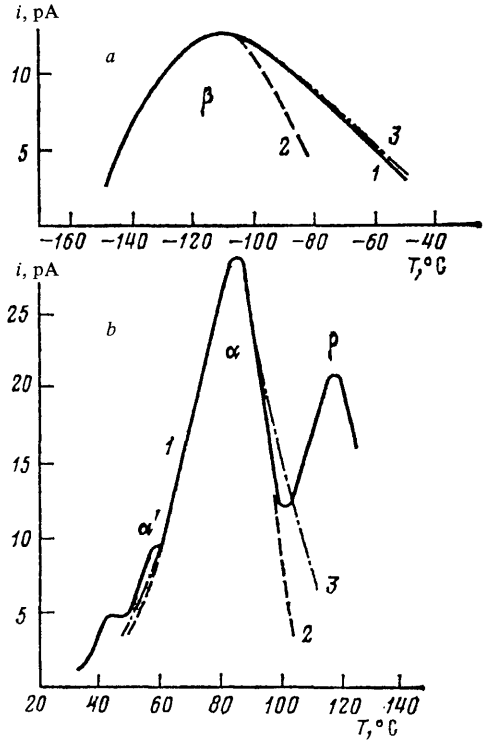


Figure 4. Temperature dependence of the TSD current of a poly(ethylene terephthalate) film thermo-electret (ETA thermogram): (*a*) low-temperature region (β relaxation); (*b*) high-temperature region (α relaxation); *1*) experimental, *2*) calculated by formula (9), *3*) calculated by formula (13).

The expressions obtained by making these assumptions [(13) and (14)] are fairly simple, but they satisfactorily describe the TSD current in the dipole group relaxation region and also, to some extent, in the dipole segment relaxation region (at temperatures below the glass transition, see Fig.4).[11] The increasing discrepancy between calculation and experiment above the glass transition temperature is not surprising, since we know that in this region the temperature dependence of the relaxation time is no longer a simple exponential but is described by the Williams–Lundell–Fermi equation[30].

By first preparing the electret and then measuring its TSD current (i.e. by carrying out an electret-thermal analysis of the polymer) we obtain not only the characteristics of the electret but also the dielectric relaxation and the molecular mobility characteristics of the polymer. A parallel study of the dielectric relaxation and of the relaxation of

mechanical stresses in the polymer establishes the interrelation between electret and dielectric characteristics and allows the electret-thermal analysis (ETA) thermograms to be interpreted.

Our measurements were carried out with poly(ethylene terephthalate),[31] polycarbonates[32–34], poly(methyl methacrylate) and methacrylate copolymers[35,36] poly(butene terephthalate),[37] poly(vinyl chloride),[38,39] polyamides and poly-imides (see p.193 of Ref.1, and also Refs.40–42), poly(vinyl fluoride) and poly(vinylidene fluoride),[43], polychlorotrifluoroethylene[25], phenol–formaldehyde resins[44], and polyalkane-imide[45].

Like the temperature plots of the dielectric losses, the ETA thermograms include at least two maxima: one in the region of the glass transition temperature, corresponding to dipole segment relaxation, and the other at lower temperatures, corresponding to dipole group relaxation (Fig.4).[32] The TSD current maxima are found at temperatures corresponding to the measurements of dielectric losses at 10^{-3}–10^{-4} Hz frequency. These frequencies are the equivalent frequencies calculated by formula (8). Measurements over a wide range of temperature and frequency (from 10^{6} to 10^{-4} Hz) show that the dielectric constant increment and the shape of the relaxation time distribution function both change with temperature. As the measurement frequency is lowered these relaxation characteristics approach the values given by the ETA. At temperatures above T_g we find a maximum in the TSD current (called the ρ maximum, see above).

In amorphous poly(ethylene terephthalate) (PETP) [31] the ETA thermogram gave one maximum near 60 °C, corresponding to the glass transition in the polymer. An increase in the degree of crystallinity of the sample produces a maximum at 82 °C which characterises the glass transition in the more ordered regions of the amorphous phase (possibly near the boundaries of the crystallites). In oriented crystalline PETP we find only a small maximum near 60 °C, but a large sharp maximum near 82 °C. Thus the relaxation time of the electret hetero-charge τ increases with the crystallinity of the sample, but even in oriented, crystalline PETP τ is small, and the surface charge gradually decays.

Polycarbonate based on *bis*-phenol A is amorphous and has a large residual polarisation[32,46]. The peak temperature on the ETA thermogram for the relaxation of the residual polarisation (α) is quite high (~150 °C), but we also find an additional maximum near 120 °C (α') which results in an immediate decay of charge after polarisation, followed by a long period of charge stability. Crystallisation lowers the secondary maximum α', thus shortening the charge stability time. A small increase in charge stability can be obtained by increasing the molecular weight of the polymer and by stretching the polymer samples to increase their orientation.

Chemical modification of the polymer (by adding triazine groups) increases the stability of the hetero-charges as well as the extent of charging by increasing the polarity of the polymer molccule[34]. The magnitude of the hetero-charge increases with both the polarity and the number of the triazine groups. The addition of norbornane groups[33,34] causes a marked increase in the glass transition temperature of the polycarbonate, thus shortening the stabilisation time of the electrets and offering a useful method of preparing electrets with a large and stable charge[47].

Poly-imides have high glass transition temperatures, and the lifetime of the hetero-charges is large in these materials, but their electrical conductivity (which is electronic) is fairly high at high temperatures[48,49]. Therefore large hetero-charges cannot be obtained in poly-imides. The lifetime of the injected charge is determined by the parameter τ_M, which under ordinary conditions (room temperature and pressure) is only 10^{6}–10^{7} s (which can be contrasted with up to 10^{9} s in polycarbonates.

In polyamides we find[50] that near the glass transition temperature the dielectric constant increment decreases very rapidly with temperature. For this reason the maximum on the ETA thermogram corresponding to randomisation of segment orientations is not usually observed. The strong peak found in the ETA thermogram is due to ionic relaxation of the Maxwell–Wagner type at the interface between the amorphous phase and the crystallites. This maximum appears in the temperature plots of dielectric measurements at frequencies below 1 Hz, and its height increases as the frequency is lowered. On the temperature scale the maximum occurs slightly above the glass transition point (α relaxation temperature). A high degree of crystallinity favours low electrical conductivity, and therefore in some of these materials (for example, polyamide-6,6) the homo-charge is very long-lived[51].

Plasticising treatment of poly(vinyl chloride) lowers the temperature of the TSD current maximum in the region of the glass transition by the same amount as it lowers the glass transition temperature[38]. The addition of plasticisers also lowers the peaks in the region of dipole group losses. A detailed analysis of the results showed that the loss of hetero-charge calculated from the area of the peak in the dipole group loss area is proportional to the increase in the elastic modulus in the temperature range from the maximum of the dipole group loss peak to the maximum of the dipole segment loss peak, i.e. it is proportional to the "deplasticising" effect.

In crystalline polyalkane-imides the dipole segment relaxation maximum decreases because the temperature increment of the dielectric constant falls to such an extent as to be undetectable unless a special technique is used to resolve the TSD current peaks[45]. In this polymer (as in polychlorotrifluoroethylene) a TSD current maximum is found at temperatures above the glass transition: it is associated with the relaxation of dipoles in the crystalline regions (α_c relaxation).

In polychlorotrifluoro-ethylene[25] several maxima are found in the glass transition region. The shape of the ETA thermogram is a function of the technology used in the preparation of the sample, and in particular of the pressure and cooling regime. The position of the maxima in the α_c relaxation region can be used to monitor the changes in polymer structure caused by different preparative regimes. Though PCTFE is a polar polymer, stable electrets (whether hetero-charged or homo-charged) cannot be prepared from it because the glass transition temperature is low and the activation energy of the α_c relaxation is low.

Vulcanised compositions of acrylonitrile and butadiene copolymers contain large (CN) polar groups. The electret hetero-charge resulting from the orientation of these groups is considerable, but the glass transition temperature lies below room temperature and therefore the hetero-charge is stable only at low temperatures. The Maxwell relaxation time is short (though it increases as the concentration of nitrile groups decreases), and therefore the homocharge is also unstable. Evidently, electrets based on vulcanised polar rubbers can be obtained only by carrying out the vulcanisation in an electric field ("chemo-electrets").[52] On the other hand, stable corona electrets can be prepared from vulcanisates of non-polar elastomers (for example, polydimethylsiloxane).[53]

In amorphous polymers such as polycarbonates and poly-imides which show a tendency towards structure formation we find (as in PETF) TSD current maxima at temperatures slightly below the glass transition temperature. Experiments

at frequencies between 10^{-1} and 10^{-4} Hz showed that the height of the maximum on the temperature plot (α') increases as the measurement frequency decreases. The height of the maximum increases with heat treatment (annealing), thermal ageing, and exposure to active media[58], which increase the hardness and brittleness of the material and lower its electrical conductivity. In every case the height of the maximum changes in the same sense as the stated parameters. After heat treatment leading to the breakdown of supermolecular formations and to the restoration of the initial properties of the polymer the height of the second maxima (α') of the TSD current also falls.

In partially crystalline polymers (PETF) the α' maximum at ~60 °C decreases as the crystallinity increases. This maximum may be associated with the motion of segments in the disordered regions of the amorphous phase, as opposed to the segments at the boundaries between the amorphous phase and the crystalline regions[31]. The latter have a limited choice of conformations, and their mobility is similarly limited: as a result, the temperature of the TSD current maximum caused by the randomisation of their orientations increases with the crystallinity of the sample.

The height of the maxima at temperatures below 0 °C (dipole group relaxation) is usually less than the value calculated from the increment of the dielectric constant at higher temperatures. This effect is part of the general increase in relaxation rates at higher temperatures.

The temperatures of the TSD current maxima due to dipole relaxation are always consistent with extrapolations of the temperatures of the dielectric loss maxima measured at 10^1 to 10^6 Hz, or with direct measurements at 10^{-3}–10^{-4} Hz frequencies (Fig. 5).

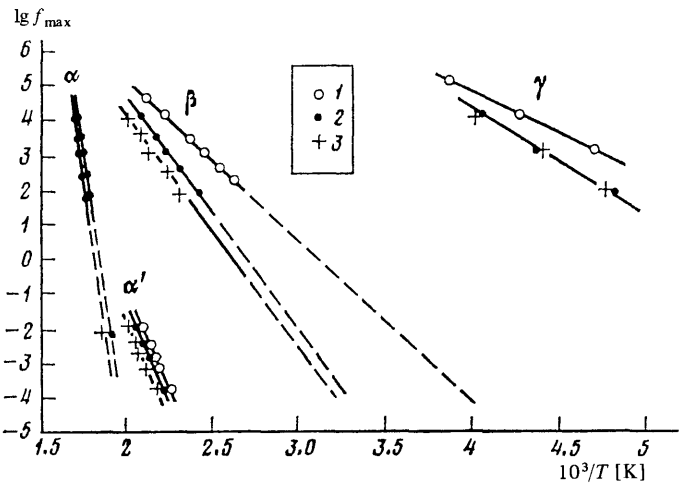


Figure 5. Logarithm of the frequency of the dielectric loss maximum against reciprocal absolute temperature for polyimides (*1* polypyromellitimide, *2* DFO, *3* BZF). The experimental points for $f_{equiv} \approx 10^{-4}$ Hz are obtained from ETA data.

In almost all the ETA thermograms we find, at temperatures higher than the polarisation temperature, a maximum in the TSD current due to the relaxation of bulk charges caused by ionic mobility (the ρ maximum). This maximum is observed, for example, at 120 °C in PETF and at 180 °C in polycarbonate. In some polymers (for example, poly-imides) this maximum is not observed: it is replaced by a monotonic increase in the TSD current due to pyro-electric effects. The height of the ρ maximum depends on the field strength, the polarisation time, and the electrode material.

As formula (14) shows, the measurement of dielectric relaxation by electret-thermal analysis can be used to determine the dielectric loss tangent: in a polymer with $E = 500$ kJ mole^{-1} and $\varepsilon = 3$ (with $E_p = 100$ kV cm^{-1}, $T = 293$ K, $b = 1$ K min^{-1}, and a detector sensitivity of 10^{-14}–10^{-15} A) the result was 10^{-6} (an improvement by two orders of magnitude on the sensitivity of conventional methods of measuring dielectric losses at audio frequencies. Furthermore, the ETA method has an enhanced resolving power due to the lower frequencies at which the measurements are made.

Table 1. Electret and dielectric parameters of a series of polymers.

Polymer	Dielectric measurements				Electret-thermal analysis			Refs.
	T_{max}, °C	Δε	E, kJ mole^{-1}	λ	T_{max}, °C	Δε	W, kJ mole^{-1}	
Dipole segment relaxation								
PC amorph.	175	0.62	586	0.40	147	0.84	197	[11]
PC cryst. (40%)	182	0.28	510	0.26	163	0.44	151	[11]
PETF cryst.	115	0.59	377	0.21	84	0.39	79	[31]
PBTF cryst.	67	1.45	356	0.12	45	1.0	64	[37]
Polysulphone	203	0.59	870	0.35	215	0.55	388	[11]
PI BZF	303	0.63	502	0.47	268	1.78	408	[1, p.193]
Dipole group relaxation								
PC amorph.	−60	0.19	54	0.17	−118	0.17	6 (10)	[11]
PC cryst. (40%)	−65	0.19	54	0.17	−113	0.17	18 (10)	[11]
PBTF cryst.	−56	0.34	67	0.17	−118	0.34	5 (11)	[37]
PETF cryst.	−40	0.5	63	0.20	−110	0.3	8 (13)	[31]
PI BZF	185	0.27	125	0.14	40	0.22	16	[1, p.193]

Notes: T_{max} for the dielectric measurements is the temperature of the ε″ maximum at 1 kHz; the W values shown in brackets were calculated by Eqn. (11), the others by Eqn. (10); PBTF is poly(butene terephthalate), PI is polyimide.

Some results obtained by ETA and by dielectric measurements respectively are compared in Table 1. They relate to a rigid (without air-gap) contact between the electrode and the electret. This type of data can be useful in studies of dipole and molecular mobility in polymers, but under real electret application conditions a gap is almost invariably present (usually, between one charged surface and its counter-electrode). If the TSD currents are measured under these conditions slightly different characteristics are obtained[23]. In particular, the TSD current associated with the ρ maximum often flows in the inverse direction as a result of the decay of the injected charge carriers. In contact-less measurements the quantity determined is often the potential difference V rather than the TSD current. The temperature dependence of V for the electret is an operational characteristic of the electret; the TSD current (measured with an air gap) is proportional to the differential of $V(T)$ with respect to time: $i(T) \propto dV(T)/dt$.[23]

In electrets formed by corona charging or by irradiation with an electron beam (rather than by thermal polarisation) measurements of thermal depolarisation give the parameters

of the traps in which the injected carriers are captured[54,55]. It should be noted, however, that these traps are often emptied by the "unfreezing" of the mobility of the corresponding structure elements, and therefore most of the TSD current peaks occur at the same temperatures as the TSD current peaks of thermo-electrets. Furthermore, the presence of injected charges in the electret gives rise to an electric field in which dipoles can become oriented if the temperature of the sample is raised, and therefore the measured TSD currents are in fact polarisation rather than depolarisation currents. According to formula (4) if $P_0 = 0$ the polarisation in the field of injected charges is proportional to $(\varepsilon_{st} - \varepsilon_\infty)/\varepsilon_{st}$. Experiments of this type on PETP have shown[23] that two maxima appear in the thermogram of corona electrets (the α and the ρ maximum), and that the ratio of their areas is equal to the ratio $\Delta\varepsilon/\varepsilon_{st} = 0.10-0.12$.

Some workers[19,55] do not specially distinguish the current maxima due to polarisation of the electret in the field of the injected charge, and they formally ascribe them to the emission of charge carriers from the traps (which is clearly incorrect). The error of this interpretation was pointed out by McGhie and coworkers[43] (among others) after a detailed study of injection and polarisation currents in poly(vinyl fluoride).

Recent work has shown[24] that the ρ maximum often occurs not at the temperature for which $\tau_M = \tau_{max}$ but at the temperature corresponding to the "unfreezing" of the mobility of the charge carriers at the crystallite boundaries (the α_c relaxation). In polychlorotrifluoro-ethylene, as in poly(vinylidene fluoride), this temperature is ~130 °C. The α_c relaxation is poorly revealed by dielectric measurements at audio frequencies, but it is clearly seen in dynamic mechanical measurements[56]. This was confirmed by our own measurements on poly(ethylene terephthalate), polycarbonate, and poly(vinylidene fluoride).

The dependence of the charges on the field intensity E_p shows a direct proportionality between P and E_p for the α maximum, as expected for dipole polarisation, whereas for the ρ maximum the plot of lg σ_{eff} against $E_p^{1/2}$ is linear, which is typical of injected charge.

We may assume that injected electrons are trapped mainly at the interface between the amorphous and the crystalline phase, where they cause orientation of the surrounding dipoles with a corresponding change in the structure of the polymer. Thus the depth of the trap is determined by the sum of the energies needed to produce the conformational changes in all the surrounding portions of macromolecules resulting from the charge carrier injection. When the electret is heated to the temperature of the α_c relaxation the traps are emptied by the "unfreezing" of the mobility of the charge carriers at the crystallite boundaries.

2. Changes in Polymer Structure Caused by Interaction with an Electric Field

The polarisation of polar polymers causes some changes in the properties and structure of the polymers. Thus, changes in mechanical properties have been reported[57]. The induced elasticity limit $\sigma_{i.e.}$ (fluidity limit) of polycarbonate increases by ~20% in thermo-electrets as compared to the unpolarised polymer. The increase in $\sigma_{i.e.}$ with polarisation time and with field strength, and the decrease in $\sigma_{i.e.}$ during storage, are consistent with the increase or decrease in residual polarisation P_0 (determined by integrating the TSD current). The following relationship is observed:

$$\sigma_{i.e.} = \sigma_0 + CP_0$$

where σ_0 is the induced elasticity limit of the initial polymer, and C is a material constant [$C = 8.82 \times 10^{10}$ N C^{-1} for polycarbonate, $C = 1.09 \times 10^{10}$ N C^{-1} for poly(ethylene terephthalate),[57] and $C = 1.24 \times 10^7$ N C^{-1} for poly(vinyl fluoride)]. The coefficient C has the dimensions of an electrostriction coefficient: it defines the effectiveness of the interaction between the residual polarisation and the mechanical properties of the polymer. The small value of C for poly(vinyl fluoride) reflects the low stability of P_0 at room temperature (at which the measurements of $\sigma_{i.e.}$ were made).

In polycarbonate electrets the velocity of sound is lower and the density is slightly higher than in the initial polymer. These changes can be ascribed to the formation of ordered, denser regions separated by less ordered and less dense regions. Similar changes in structure take place during lengthy heat treatment of the polymers at temperatures close to T_g;[58] these changes are accelerated if the ordering process is assisted by an electric field. The thermophysical properties of the polymer are affected at the same time. A sharp increase in the height of the specific heat maximum (as compared with the unpolarised material) is observed by differential scanning calorimetry on the thermograms of electrets near T_g. For example, in poly(vinyl chloride) the enthalpy ΔH increases 1.5-fold. This thermal effect is due to the breakdown of the residual polarisation[50].

Table 2. Piezo-electric properties of polymer electrets.

Polymer	T_p, °C	E_p, kV cm^{-1}	t_p, h	d_{31}, pC N^{-1}	d_{33}, pC N^{-1}	τ*, days	Refs.
PC amorph.	145	300	2	0.10	0.10	254	[10, 67]
PC cryst. (40%)	145	200	3	0.11	0.10	10^3	[10]
PA-11	—	—	—	0.5	—	10^3	[67]
PA-12	160	60	2	0.11	0.2	2	[10]
PA-6,6	160	60	2	0.11	0.3	—	
PVC	80	250	2	1.7	1.7	$1.1 \cdot 10^5$	[10, 62]
PAN	115	200	2	0.62	4.1	640	[62]
PETF amorph.	100	100	2	1.5	—	0,06	[10]
PETF cryst.	120	200	3	0.01	—	—	[10]
PVF	83	220	2	2.2	4.0	500	[76]
PVDF α form	90	100	2	0.66	2.7	10^3	[76]
PVDF β form (60% cryst.)	80	600—1000	0.5	15—25	6.3—20	10^5	[76]
PVDF with additions of LTZ** (21 vol%)	120	120	0.5	4.2	—	—	[83]
Poly-3,3(dichloro-methyloxycyclo-butane)***	120	250	1	30	—	—	[66]

*Relaxation time of the piezo-modulus d.
**Lead titanate zirconate.
***Pentaplast, or Pentone.

Mechanical deformation of polar polymers produces mechano-electrets[1,59-63] in which the size of the charge increases with the degree of deformation. Mechano-electrets have well developed piezo-electric properties[62], stronger than those of thermo-electrets made from the same polymers[63]. The orientation of the macromolecules during deformation induces a preferred orientation of the dipoles (with their polar groups normal to the deformation plane). The increases in the induced elasticity limit and in the mechanical strength of the polymer samples resulting from polarisation[57] are the inverse effects of the formation of mechano-electrets.

In crystalline polymers [poly(vinylidene fluoride), polyamide-11] changes in structure of the crystallites can be produced by a polarising field. In poly(vinylidene fluoride) the crystalline α form is converted into the β form[64] by the rotation of the dipoles (CF_2 groups) round the axis of the macromolecule chain. A theoretical analysis[65] has shown that this rearrangement is assisted by the simultaneous rotation of all the CF_2 groups in the chain, which gives the lowest total free energy. The dependence of the polarisation P on the field strength E_p for a slowly changing field (10^{-1}–10^{-4} Hz) has a typical relaxation form with a hysteresis loop (as in ferroelectric materials). Similar electret properties have been reported for poly-3,3-*bis*-chloromethyloxyethane (Pentaplast),[66] polyamide-11,[67] and the copolymers of vinylidene fluoride and trifluoro-ethylene[68,69].

Unfortunately, studies of hysteresis phenomena have not been made on other polymers. In view of the relaxation form of the molecular mobility we may assume that ferroelectric phenomena are present to a greater or lesser extent in all polar polymers.

Changes in structure of polyacrylonitrile after polarisation have been studied by i.r. spectroscopy and X-ray structural analysis[61]. This work has revealed ordering effects in the segments and an increase in the density of ordered regions. Similar effects were observed when the sample was annealed without an electric field, but in a lesser degree. The authors point out[61] the similarity between the changes in structure of polyacrylonitrile and those of polycarbonate[57].

IV. PIEZO- AND PYRO-ELECTRIC PROPERTIES OF ELECTRETS

1. Piezo-electricity in Polymer Electrets

The piezo-effect in electrets[70–81] is due to the change in the surface charge density caused by deformation of the polymer[70]:

$$d_{33} = \frac{dP}{dF} - 2\eta \frac{\sigma_{eff}}{E_{el}} \qquad (15)$$

where F is the load, η is Poisson's ratio, E_{el} is the elastic modulus, and d_{33} is the piezo-modulus of the planar polymer electret under compression (the polarisation axis is assumed to coincide with the deformation axis "3").

Experiments on ceramic electrets have shown that the second term of Eqn.(15) is too small to account for the observed piezo-effect. However, in polymer electrets the elastic modulus is small, and in rubber "chemo-electrets" the piezo-effect is fully accounted for by the second component[52,71].

Later work with a large number of polymers (see p.145 of Ref.1) showed that the piezo-effect tends to increase with the polarity of the polymer, whereas its stability increases with the rigidity of the macromolecular chain. A theoretical analysis[10] demonstrated that if the dielectric constant is unaffected by the deformation (i.e. if the electrostriction coefficient is small) the piezo-modulus under expansion d_{31} reflects exclusively the changes in geometric shape of the sample, and is given by

$$d_{31} = -(1-\eta) P_0/E_{el}$$

whereas under compression

$$d_{33} = -2\eta P_0/E_{el} . \qquad (16)$$

These relationships are useful for predicting the practical value of electret devices based on the piezo-electric properties of polymers. Knowing E_{el} and the P_0 value given by integration of the TSD current or calculated by formula (7) we can find the piezo-modulus. Calculated and experimental values of the piezo-modulus d_{31} are compared in Table 2.

Broadhurst and Davies[72] allowed for the Onsager internal field. Assuming that the formation of residual polarisation orients the dipoles along the field at an average angle θ to the direction of the polarising field, they obtained the expression for P_0

$$P_0 = (\varepsilon_\infty + 2) N \mu_0 \langle \cos\theta \rangle / 3 \qquad (17)$$

which gave the formula for $d = dP_0/dF$

$$d = -P_0 \frac{\varepsilon_\infty}{3} \alpha \qquad (18)$$

where α is the volume compressibility. Since under compression $\alpha = (1/V)(dV/dE) = 2\eta/E_{el}$, and since $\varepsilon_\infty \cong 3$ for poly(vinyl chloride), for which formula (18) has been shown to be valid[73], we arrive at an expression identical to Eqn.(16).[10]

Eqns.(16) and (17) are convenient for electrets with a residual polarisation consisting of oriented and "frozen" dipoles. It is found experimentally[74] that non-polar polymers with an injected homo-charge σ_p also show a piezo-effect, especially under flexural deformation, though the piezo-modulus is small.

In poly(vinylidene fluoride) the piezo-effect is so large as to require special discussion. Poly(vinylidene fluoride) (PVDF) is a polar polymer characterised [like poly(vinyl fluoride)] by a low glass transition temperature (below room temperature). Therefore under normal conditions the polymer in the amorphous phase is in a highly elastic state, and thermo-electrets made from this material are unstable. Injected charge carriers (homo-charges) are captured in traps at the boundary between the amorphous and the crystalline phase, from which they can be freed only by the "unfreezing" of the mobility of the macromolecules on the crystallite surfaces (α_c relaxation). This effect is confirmed by dynamic mechanical measurements[24], and is analogous to the corresponding process in polytetrafluoro-ethylene (a typical electret material).

We can assume that charge carriers trapped near the surface can survive for a long time ($\geq 10^{10}$ s), and generate a strong internal field in which the dipoles are oriented[10]. The application of a mechanical load to a dielectric with oriented dipoles produces a piezo-effect whose magnitude depends on the injected charge σ_p (measured by integrating the TSD current in the region of the α_c relaxation), on the depth of injection l, on the sample thickness L, and on the polarisability (defined as $\Delta\varepsilon = \varepsilon_{st} - \varepsilon_\infty$). The piezo-modulus under expansion is

$$d_{31} = \frac{(1-\eta)}{E_{el}} \frac{\Delta\varepsilon(\alpha)}{\varepsilon_{st}} \sigma_p \frac{l}{L+l} .$$

Inserting $l = 1$ μm with $L = 20$ μm and $\varepsilon_{st} = n_\lambda^2 + \Delta\varepsilon(\alpha) = 2.2 + 6.2 = 8.4$ for a non-oriented film of PVDF in its less polar, crystalline σ form, with $\sigma_p = 0.057$ C m^{-2} and $E_{el} = 1.1 \times 10^9$ Pa, we obtain $d_{31} = 1$ pC N^{-1}. After orientation the parameter $\Delta\varepsilon(\alpha)$ increases to 8–11, and σ_p increases to 1.48 C m^{-2} for polarising fields up to 450 kV cm^{-1}. In this case d_{31} increases to 22–30 pC N^{-1}, which corresponds to the highest experimentally observed values of d_{31}.

This theoretical model by allowing for the role of injected charges brings all the polymer electrets into a coherent group. It can be used to calculate the change in structure of PVDF in an electric field in terms of changes in ε only. Similar views have been expressed by other workers[67,76,77].

However, wide acceptance has been gained by the view[78–80] that the piezo-effect in PVDF and in the copolymers of vinylidene fluoride is due mainly to spontaneous polarisation

in the crystallites of the β form, which is formed from the crystalline α form by the orienting effect of stretching the sample or under the influence of very strong electric fields ($\sim 10^8$ V m^{-1}).

Other workers[74,81] have allowed for the crystallites of the polar, spontaneously polarised β form dispersed in the amorphous matrix as well as for the change in dielectric constant produced by the deformation. This approach gave the following expression for the piezo-modulus d in PVDF:

$$d = \frac{P_0}{E_{el}}\left[\frac{\varepsilon_{cr}}{2\varepsilon+\varepsilon_{cr}}\left(\frac{\varkappa}{\varepsilon}-\frac{\varkappa_{cr}}{\varepsilon_{cr}}h\right)+2\eta\right]+v\left(\frac{3\varepsilon}{2\varepsilon+\varepsilon_{cr}}\right)h \qquad (19)$$

where the subscript "cr" refers to the polymer in the crystalline form, v is the volume fraction of the crystalline phase, $h = 5E_{el}/[3E_{el} + 2E_{el}(cr)]$, and $\varkappa$ is the electro-striction coefficient, equal to $E(\partial\varepsilon/\partial F)$. The calculation shows that the component d [due to the change in shape of the sample and related to the Poisson ratio by Eqn.(19)] accounts for ~78% of the piezo-effect[81]. However, the parameter P_0 is identified[81] with the spontaneous polarisation of the electret in the crystalline β form rather than with the polarisation in the field of the injected charge.

Thus the piezo-effect in polymer electrets may be due to the change in surface density of the homo-charge caused by deformation ($d\sigma_p/dF$), the change in density of the residual polarisation P_0 (dP_0/dF), or the "true" piezo-effect in the spontaneously polarised particles (in PVDF these particles consist of polarised crystallites of the β phase).

These spontaneously polarised particles need not even (in general) be particles of the polymer: they could be introduced as a powdered inorganic ferro-electric. In this case the piezo-electric properties of the resulting composite materials can be extremely high. By combining a suitable content of ferro-electric powder with a polymer having adequate polarity and intrinsic piezo-electric properties materials with very favourable characteristics have been obtained[82-85]. The production of polymeric or composite piezo-elements is incomparably simpler than the preparation of ceramic devices, and the piezo-sensitivity per stage of the former ($g_{33} = d_{33}/.\varepsilon\varepsilon_0$) is 10–100 times greater than in the ceramic ferro-electric devices because of the lower ε values in polymers.

2. Pyro-electricity in Polymer Electrets

Pyro-electricity appears as a result of changes in polarisation P or in the density of injected charges produced by changes in temperature.

The pyro-coefficient p, which characterises the change in charge density of the dielectric produced by a change in temperature of one degree, is directly proportional to P_0 and to the volume thermal expansion coefficient α:[73]

$$p = -\frac{\varepsilon_\infty}{3}\alpha P_0 .$$

The pyro-effect associated with σ_p is usually small. In the case of polymers containing a ferro-electric component [poly(vinylidene fluoride)] the pyro-effect is described by a formula derived from a mixture of a ferro-electric and a non-polar substance[81]:

$$p = P_0\left[\frac{\varepsilon_{cr}}{2\varepsilon+\varepsilon_{cr}}\left(\frac{\lambda}{\varepsilon}-\frac{\lambda_{cr}}{\varepsilon_{cr}}\right)-\beta\right]+v\left(\frac{3\varepsilon}{2\varepsilon+\varepsilon_{cr}}\right)P \qquad (20)$$

where $\lambda = \partial\varepsilon/\partial T$ is the temperature coefficient of the dielectric constant, and β is the linear thermal expansion coefficient. It was found experimentally that the component of p due to the volume change [and associated with the coefficient β in Eqn.(20)] makes a 50% contribution to the pyro-effect in PVDF.

Composite materials based on polymers with added ferro-electrics offer large values of the pyro-coefficient p. Some recent results are summarised in Table 3.

V. APPLICATIONS OF POLYMER ELECTRETS

Electrets can find applications: 1) as dielectrics, with an added external electric field, 2) as dielectrics, with an internal polarisation, 3) as piezo-electric materials, and 4) as pyro-electric materials.

Table 3. Pyro-electric properties of polymer electrets.

Polymer	E_p, kV cm^{-1}	T_p, °C	$10^5 p$, C m^{-2}K^{-1}	Refs.
PVC	320	90	0.11	[73]
PAN	215	109	0.054	[73]
PAN	—	—	3.9	[96]
PVDF, not oriented, α-form	300	100	2.4	[76]
PVDF, uniaxially oriented, β-form	2200	20	2—20	[76]
PVDF, biaxially oriented, β-form	2200	20	2,7—8.0	[76]

As dielectrics (with an external electric field) electrets are widely used in filters, for controlling electron beams (and in particular for focussing electron beams), and in electro-mechanical transducers (microphones, pick-ups, etc.). The most widely used of these devices is the electret condenser microphone, currently manufactured on a scale of millions per annum. The use of electrets has greatly simplified microphone design, allowing a reduction in size to ~5 mm coupled with improved properties (for example, the linearity region of industrially produced electret microphones extends from 50 to 16000 Hz).[2,86-88] Special electret microphones for studying ultrasound and infrasound have also been described[89]. Electret fibre filters[90], developed outside the Soviet Union under the name "filtret",[91] are now widely used: they are cheap, much more efficient than previous fibre filters, and they offer excellent protection against airborne industrial or radioactive dust.

The incidence of thrombosis has been reduced by using artificial blood vessels and artificial heart components with electret properties[92].

In their second function electrets can be used as a very special type of electric cell. A temperature rise (for example, in a fire alarm device) may give a TSD current sufficient to activate a radio transmitter (see p. 204 of Ref.1).

As piezo-electric materials[93] polymer electrets have been used in stereo headphones, acoustic pick-ups[94], and igniters, and also in fans. Over 40 different applications of piezo-electric poly(vinylidene fluoride) polymer film have already been patented[76]. Applications in hydro-acoustics, in switching systems for fibre optics, in the generation of focussed ultrasonic signals, and in the prevention of fouling of ships' hulls by marine plants and molluscs[95] are especially interesting.

Likely future pyro-electric applications of polymer electrets (for example, based on acrylonitrile) include the direct conversion of solar into electrical energy[96], night viewing with infrared radiation [poly(vinylidene fluoride)], and various forms of pyro-electric detector and other devices[76,93].

* * *

In conclusion we note that the prospects of more widespread applications of polymer electrets are good. New uses are being discovered every year, in very different branches of technology. We should also stress that only a small number of polymer electret materials has been exploited in practice so far. For the production of external electric fields the following materials have been used most widely: polytetrafluoro-ethylene, the tetrafluoro-ethylene–hexafluoropropene copolymer, polycarbonate, and poly(methyl methacrylate), whereas polypropene, poly(chlorotrifluoroethylene), and poly(methyl siloxane) are beginning to find practical applications. Materials used in practical piezoelectric devices include poly(vinylidene fluoride), poly(vinyl chloride), and composite polymer materials containing a ferro-electric ceramic filler (lead titanate zirconate).

We can expect practical applications of polymer electrets in pyro-electric devices, and the development of an increasingly wide range of polymers for use in electric field generators and in piezo-electric devices (polyamides, polysulphones, and vinylidene fluoride copolymers[97]). Further developments in the modification of the physico-mechanical properties of polymers by the application of electric or magnetic fields can also be expected.

The study of the influence of an external electric field on the structure of polymer electrets is still in its initial stages[98,99].

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Molecular Photocatalytic Systems for Solar Energy Conversion: Catalysts for the Evolution of Hydrogen and Oxygen from Water †

K.I.Zamaraev and V.N.Parmon

This review is devoted to recent advances in the development and study of homogeneous and heterogeneous catalysts for the reduction of water to molecular hydrogen and its oxidation to molecular oxygen. The production of micro-heterogeneous systems for photocatalytic charge separation is also discussed. 114 references.

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I. INTRODUCTION

Mankind's total annual energy consumption now stands at the enormous value of ~10^{17} kcal, and is still rising rapidly, doubling every 15–20 years[1–3]. However, our reserves of mineral fuels which provide the main input to the energy balance (~80% of the primary energy resources, including ~60% of petroleum and gas) are strictly limited: the total energy equivalent of the explored reserves of these fuels is estimated to be[3–5] 10^{19}–10^{20} kcal. Thus the search for alternative sources of energy is a very important problem.

It is thought that for the immediate future the energy requirements of the world community will be satisfied by an increase in the mining and conversion of coal (including its conversion into artificial liquid fuel), and in the use of nuclear sources of electrical energy and heat. The raw materials required by these two branches of energetics are assured for at least one century. In both cases the level of scientific and technological development already reached is high enough to make early practical exploitation a real possibility. However, we should not forget that a substantial increase in the use of coal and of nuclear fuel will present a number of as yet unsolved problems arising from possibly detrimental effects on the environment. For example, the combustion and treatment of coal will require the development of cheap purification plant to prevent the accumulation of sulphur oxides, carcinogens, and other harmful substances in the atmosphere. There is even a danger that at the expected rate of increase of energy

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consumption the anthropogenic heat evolution from the use of fossil and nuclear fuels may reach several per cent of the total heat balance of the Earth by the middle of the next century, with unpredictable effects on the Earth's climate[6]. Equally unpredictable are the consequences of enriching the atmosphere in carbon dioxide (unavoidably produced by the combustion of organic substances).

For the more distance future we must look to two sources of energy available almost without limit: thermo-nuclear energy and solar energy[1]. Neither of these sources can yet be widely exploited because the level of scientific and technological development is inadequate at present in both cases. However, there is every reason to expect very rapid progress. Basic research on a controlled thermo-nuclear reaction is in progress. Although this reaction has not yet been realised experimentally, the potential advantages of thermo-nuclear synthesis as a source of energy have been widely discussed for many years. On the other hand the possibilities offered by solar energy are less clearly characterised, though it is known that the energy content of the Sun's rays which reach the Earth is far in excess of even the highest estimates of mankind's increasing requirements[1-3,7,8]. The only problem is to learn how to use this energy effectively.

There can be no doubt that in the near future the traditional sources of energy will continue to play a major role in the overall energy balance of mankind. Nevertheless, even the International Energy Conference (an organisation traditionally opposed to the use of solar energy) admits the possibility of a significant increase in the direct exploitation of solar energy: in particular, it is expected that by the year 2020 up to 10–15% of the world's energy requirements will be provided by solar energy converters[2].

One of the most promising methods of utilising solar energy is its direct conversion into chemical fuel energy[1,9-11]. Storing the Sun's energy in the form of chemical fuels would overcome the most serious obstacle to the widespread use of solar energy (its dependence on seasonal, meteorological, and other natural conditions) as well as making the energy available in a more concentrated and generally usable form (a high-level chemical energy source).

In principle any chemical process in which free energy is accumulated can be used for the conversion of solar energy. The most attractive, at present, are the reactions which produce high-energy fuels (hydrogen, hydrocarbons, alcohols and carbohydrates, hydrazine, ammonia, etc.) from water and atmospheric gases, which offer a readily available and almost inexhaustible raw material (see, for example, the recent reviews in Refs.12 and 13). The advantages of these reactions include the high energy content of the resulting fuel (the combustible–oxidiser (oxygen) pair of chemical substances), and also the possibility in principle of achieving a relatively high efficiency (up to ~30%) in the conversion of solar energy[14-16]. We should stress that the production of all these fuels takes place *in vivo* in plants and micro-organisms (either by photosynthesis, followed by fermentation of the products to hydrogen, methane, alcohols, etc., or by atmospheric nitrogen fixation).

However, these reactions do not proceed spontaneously in sunlight outside the living organism. They require the development of *photocatalytic* systems, consisting of *photocatalysts* (for the photochemical step) and *ordinary catalysts* (for the subsequent dark reaction steps giving the energy-rich chemical substances).

Photocatalysts are substances which can induce (by the absorption of light quanta) chemical reactions between the components of a reaction by undergoing repeated chemical interactions to form an intermediate and regenerating themselves after each interaction. (The term "photocatalyst" is often replaced, in published papers, by the term "photosensitiser", on the assumption that the two are synonymous. It would be more correct to reserve the term "photosensitiser" for substances which induce reactions by energy transfer to the reactants rather than by forming chemical intermediates with them.)

The most interesting of the fuel-producing processes listed above is the production of hydrogen by the decomposition of water. Hydrogen is one of the preferred (and ecologically clean) chemical fuels for energy production in the future. It is also a valuable raw material for the chemical industry, used in large quantities for the catalytic reduction of carbon dioxide and molecular nitrogen to give all the fuels listed above. Lastly, existing information on the chemical reaction mechanisms suggests that the photocatalytic decomposition of water should be the most easily realisable of all the reactions for storing solar energy as fuels.

Some definite advances in the development of photocatalytic systems for the decomposition of water into hydrogen and oxygen have already been reported. The systems can arbitrarily be classified into two groups: semiconductor systems and molecular systems.

Semiconductor systems rely on massive or on finely divided semiconductors as photocatalysts (mainly oxides, phosphides, arsenides and chalcogenides of the transition metals). By using these substances solar energy has been converted into chemical fuel energy with reasonable efficiencies (up to 1–2%) (see the pioneering paper by Fujishima and Honda[17], and also the most recent reviews[18-21] and their references). The efficiency of semiconductor photocatalytic systems for the decomposition of water will probably be further increased by research now in progess. A detailed analysis of the present situation in the field of semiconductor photocatalysis will be found in the same reviews[18-21].

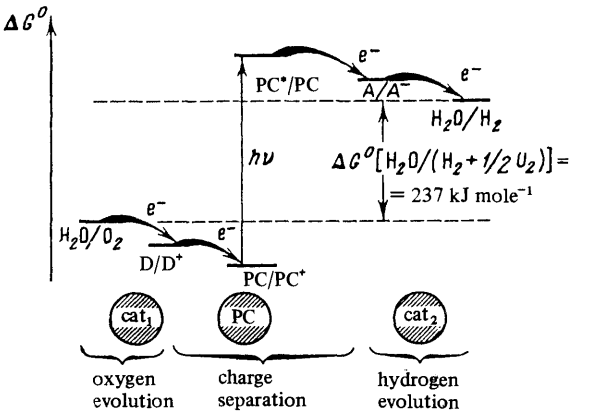


Figure 1. Energy diagram for the decomposition of water in a molecular photo-catalytic system; ΔG° is the change in free energy for the process, the curved arrows show the electron transfer paths.

Molecular photocatalytic systems attempt to reproduce (or model) the natural photosynthesis schemes. Work on these systems began later than on the semiconductor systems,

and has not yet produced really significant advances. However, since we know that the efficiency of the conversion of solar energy by the molecular systems used in natural photosynthesis is quite high (up to 6–10% for the relatively complex reaction between CO_2 and H_2O [22,23]) there is every reason to expect the early development of efficient artifical converters for the much simpler water decomposition reaction.

Recent progress in the development of molecular photocatalytic systems for the decomposition of water have been discussed in a number of reviews[21,24–29], including one by the present writers[12]. Among the papers published since our review[12] the most noteworthy are Refs.30 and 31 (see also Refs.21 and 25), which claim the development of the first artificial molecular system capable of yielding the full cycle of decomposition of water into hydrogen and oxygen under the influence of visible light (albeit with a modest efficiency).

The water decomposition schemes most often considered include three steps (see Fig.1): charge separation, i.e. the production (under the influence of light and in the presence of the photocatalyst PC) of relatively strong chemical oxidisers (D^+) and reducers (A^-)

$$D + A \xrightarrow[PC]{h\nu} D^+ + A^- \qquad (1)$$

followed by catalytic processes for the evolution from water of oxygen by the oxidisers D^+

$$4D^+ + 2H_2O \xrightarrow{cat_1} 4D + 4H^+ + O_2\uparrow \qquad (2)$$

and of hydrogen by the reducers A^-

$$2A^- + 2H^+ \xrightarrow{cat_2} 2A + H_2\uparrow . \qquad (3)$$

Light is not needed for the last two steps. The overall process is described by the equation

$$2H_2O \xrightarrow[cat_1,\ cat_2]{h\nu,\ PC,\ D,\ A} 2H_2 + O_2 .$$

Thus efficient catalysts of three types must be developed in order to realise the decomposition of water into hydrogen and oxygen by sunlight in the presence of a molecular photocatalytic system: catalysts for charge separation in visible light, catalysts for oyxgen evolution from water by one-electron oxidisers, and catalysts for hydrogen evolution from water by one-electron reducers. For example, in the proposed[30,31] molecular photocatalytic system the compounds PC, A, cat_1, and cat_2 are, respectively, the *tris*-bipyridyl complex of ruthenium(II) [$Ru(bipy)_3^{2+}$], the organic bication *N,N'*-dimethyl-4,4'-dipyridine ("methylviologen", MV^{2+}), colloidal ruthenium dioxide, and colloidal platinum. The photocatalyst PC also acts as the intermediate donor D.

In this review we shall discuss the main results of recent work carried out in our laboratory since the publication of our last review[12] on the development and characterisation of catalysts for all three steps in the decomposition of water by molecular photocatalytic systems: we shall begin with the hydrogen evolution step, which is the most developed at present.

II. EVOLUTION OF HYDROGEN FROM WATER

The one-electron reducers A^- formed in the charge separation step [reaction (1)] can evolve hydrogen from water by reaction (3) only in the presence of special catalysts. Even the earliest workers[32–38] had suggested several possible catalysts for this process: supported[39–41] or colloidal precious metals (references given below), and biological enzymes (hydrogenase and nitrogenase[28,34,39,42–48]). To compare the relative merits of these catalysts in practical photocatalytic systems we need detailed quantitative information on their catalytic activity and stability, and also on the dependence of these properties on the formation conditions of the catalyst. Studies of this type are now being made in a number of laboratories on colloidal metal catalysts (see, for example, Refs.21 and 41–56, and their lists of references).

In the following sections we shall discuss two types of catalyst for the evolution of hydrogen from water: 1) highly dispersed precious metals, stabilised in polymer globules and grandules which are permeable to the reducing agent and to water molecules, and 2) heteropolyanions (compounds containing several transition metal ions which can be fully and reversibly reduced by accepting two or more electrons). Thus the heteropolyanions can be treated as structural and functional models of the hydrogenase and nitrogenase enzymes, whose active centres also contain several transition metal ions and are reduced reversibly by several electrons.

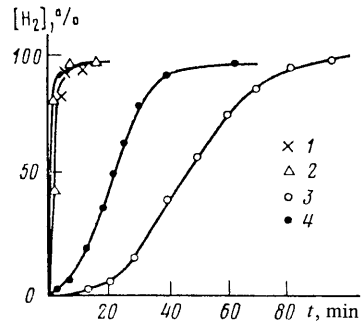


Figure 2. Kinetics of hydrogen evolution (in per cent of the stoichiometric yield) from a 1.5×10^{-2} M solution of VSO_4 in water in the presence of various catalysts: *1*) [Rh·en]Cl_3, *2*) and *3*) Rh–PEI of composition Rh : N ≅ 1 : 2 and 1 : 4 respectively, *4*) $[Rh(en)_2Cl_2](ClO_4)$. Volume of solutions 20 cm^3, amount of rhodium in solution ~10^{-5} g-atom, pH of solutions adjusted to pH : 0 by H_2SO_4, temperature 298 K.[57]

1. The Rhodium–Ethylenediamine and Rhodium–Polyethyleneimine Systems

We have shown[57] that the coordinationally unsaturated complexes of rhodium(III) with ethylenediamine (en) and with its polymeric analogues (polyethyleneimines) are active catalysts for the evoluation of hydrogen from water by one-electron reducers such as V^{2+}(aq), Cr^{2+}(aq), and the cation radical methylviologen (MV^+), by the reaction

$$2A^- + 2H^+ \xrightarrow{cat_2} 2A + H_2\uparrow$$

or

$$2A^- + 2H_2O \xrightarrow{cat_2} 2A + H_2\uparrow + 2OH^- \qquad (3a)$$

The most interesting in practice are the heterogeneous catalysts based on polymers: branching polyethyleneimine (PEI) of molecular weight ~20 000 and the commercial ion exchanger AN-221 (granulated, partially cross-linked polyethyleneimine).

Studies by ESR, X-ray photo-electron spectroscopy (XPS), and optical spectroscopy in the visible and u.v. regions have shown[58] that in the initial forms of the catalyst based on monomeric ethylenediamine almost the whole of the rhodium is present as the rhodium(III) complex, whereas in catalysts based on polyethyleneimine up to 5% of the rhodium (depending on the preparative conditions) can be present as a rhodium(II) compound, the remainder being in the form of a rhodium(III) compound. It was shown that whereas with monomeric ligands the initial complexes can have the composition Rh : N = 1 : 6, 1 : 4, and 1 : 2 (the latter complexes being obtained only in mixtures with Rh : N = 1 : 4 complexes), in the case of polymeric deprotonated ligands initial complexes of composition Rh : N = 1 : 4 and 1 : 2 are formed. By varying the metal–ligand ratio in the synthesis we can obtain heterogenised metal–polymer complexes predominantly of the Rh : N = 1 : 2 or 1 : 4 composition.

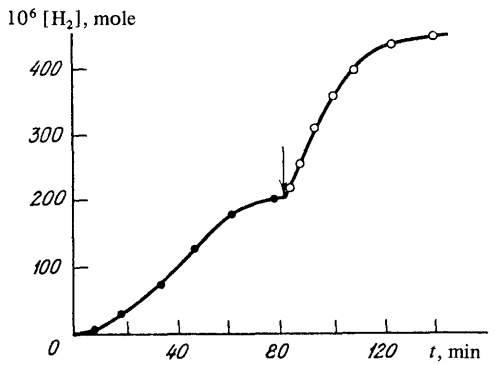


Figure 3. Kinetics of the evolution of hydrogen from a 1.5×10^{-2} M solution of VSO_4 in water in the presence of the polymer catalyst Rh–PEI of composition Rh : N ≅ 1 : 4; other conditions as in Fig. 2, the arrow denotes the addition of the second portion of VSO_4.

The addition of complexes of rhodium with ethylenediamine or polyethyleneimine to solutions of reducing agents such as V^{2+}(aq) (redox potential $E_0 = -0.25$ V relative to the NHE) and Cr^{2+}(aq) ($E_0 = -0.4$ V) causes evolution of molecular hydrogen. Typical H_2 evolution kinetic curves are shown in Fig. 2. They are S-shaped, with an initial induction period during which the reaction gradually accelerates. The induction period probably corresponds to the formation of the active forms of the catalyst (possibly highly dispersed particles of metallic rhodium, see below). The slowing down of the reaction at long times indicates depletion of the reducing agent. Thus, at the plateau of Fig. 2 the amount of hydrogen evolved is almost exactly 100% of stoichiometric for reaction (3) or (3a). At the same time by adding reducing agent at its original concentration when the reaction has come to an end we can produce a renewed evolution of hydrogen in which the slope of the kinetic curve is either the same as that of the initial curve or greater (see Fig. 3). As Fig. 2 shows, both with the monomeric and with the polymeric ligand the activated catalysts prepared from complexes of composition Rh : N = 1 : 2 have a much higher activity than those prepared from complexes of composition Rh : N = 1 : 4. In the presence of monomeric coordinationally unsaturated complexes of composition Rh : N = 1 : 6 no hydrogen is evolved by the reaction with V^{2+}(aq) or Cr^{2+}(aq).

According to X-ray structural analysis and XPS results[58] the activation of the monomer complexes of composition Rh : N = 1 : 2 causes complete reduction to finely divided metallic rhodium. The formation of a phase of metallic rhodium of very small particle size was observed also in all the activated polymer catalysts. Electron microscopic studies of the particles of metallic rhodium in polymer catalysts revealed a complex size distribution, depending on the catalyst preparation conditions. However, in every case we can detect a large number of small (10–30 Å) particles partially coalescing into larger and irregular formations. Evidently, the metallic rhodium is responsible for the catalytic activity of all the catalysts based on ethylenediamine and polyethyleneimine.

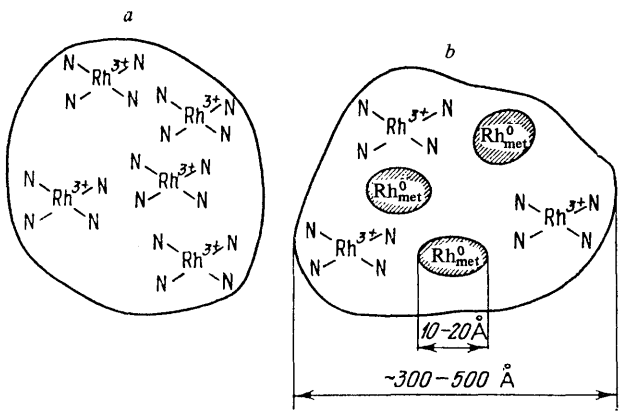


Figure 4. Structure of the Rh–PEI catalyst of composition Rh : N ≅ 1 : 4 (*a*) before and (*b*) after activation.

However, in the activated polyethyleneimine catalysts of composition Rh : N = 1 : 4 not all the rhodium ions are reduced to the metal. The reflection spectra of these catalysts in the u.v. and visible regions indicate the presence of large amounts of unchanged initial complexes of composition Rh : N = 1 : 4.[58] The XPS spectra also suggest that most of the rhodium on the sample surface is in the form of Rh^{3+} ions rather than of metal. A schematic model of the activated catalysts consistent with the results of various physicochemical methods of analysis is shown in Fig. 4. We note that the size of the finely divided metal particles in the polymer globule is strongly dependent on the catalyst activation conditions. Thus, an increase in the pH of the solution in which activation takes place causes a marked decrease in particle size.

The maximum rate (α) of hydrogen evolution (i.e. the rate in the region of maximum slope of the S-shaped kinetic curves) referred to 1 g-atom of added rhodium[59] was taken as the quantitative characteristic of the catalytic activity. Values of α for catalysts prepared by different methods are compared in Table 1. In the case of the most active catalysts

(Nos.7, 8, 11, 12) the tabulated value is not the parameter α but its lower limit. This is because reaction (3) had almost gone to completion when the first gas sample was taken for chromatographic analysis, and its rate could not be measured to better than a lower estimate.

Table 1. Catalytic activity (α, mole H_2 mole^{-1} Rh h^{-1}) of complexes of rhodium with polyamines towards the evolution of hydrogen from 1.5×10^{-2} M solutions of VSO_4 in water at 298 K (pH adjusted with H_2SO_4). [59]

No.	Initial form of catalyst	pH	$[V^{2+}]/[Rh^{3+}]$	α
1	$[Rh(en)_3](ClO_4)_3$ (Rh : N = 1 : 6)	0	30	<0.01
2	$[Rh(en)_2Cl_2](ClO_4)$ (Rh : N = 1 : 4)	0	6	5.0
3	ditto	1	6	2.9
4	»	2	6	1.6
5	»	3	6	0.75
6	»	4	6	0.15
7	[Rh·en]Cl_3 (Rh:N≈1:2)	0—2	30	>300
8	ditto	2	240	>1700
9	Rh — PEI (Rh : N ≈ 1 : 4)	0	30	16
10	ditto	2	30	0.82
11	Rh — PEI (Rh : N ≈ 1 : 2)	0	30	>400
12	ditto	2	30	>300
13	Rh — AN-221 (~7%Rh, Rh : N ~ 1:3,4)	2	120	8.7
14	ditto	2	120	640*

*Catalytic granules ground to a powder of particle size less than 0.1 mm; initial size of the granules 2 mm.

It is clear from Table 1 that the catalysts prepared from complexes (with monomeric ligands) of composition Rh : N = 1 : 2 have an activity several orders higher than the complexes of composition Rh : N = 1 : 4 with the same ligands. The lower activity of the catalysts prepared from the latter complexes can be ascribed to the less complete conversion of the ionic forms of rhodium into highly dispersed metal particles. Thus the activation of the monomer complex of composition Rh : N = 1 : 2 is accompanied by a visible precipitation of metallic rhodium in the solution, whereas during the activation of the complexes of composition Rh : N = 1 : 4 the precipitation of metallic rhodium is undetectable.

The dependence of the catalytic activity α on the concentration of H^+ ions was studied [59] for monomer complexes of composition Rh : N = 1 : 4. We see from Table 2 that the parameter α for these catalysts increases monotonically with the concentration of H^+ in the solution where reaction (3) is taking place after activation of the catalyst. However, this increase in α is much slower than expected from the law of mass action for a reaction in which the H^+ ion appears in the rate-limiting step. Further work is needed to explain the observed dependence of α on $[H^+]$.

As in the case of the monomer complex, changing from a polymer complex with a ratio Rh : N = 1 : 4 to a polymer with Rh : N = 1 : 2 causes a large increase in catalytic activity. Again, as in the case of the monomer catalyst of composition Rh : N = 1 : 2, and for the same reason, we could only obtain a lower estimate of α for the polymers with Rh : N ≅ 1 : 2.

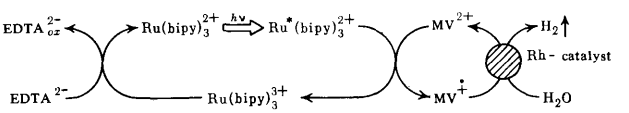
In the catalyst Rh—AN-221, consisting of granules of the AN-221 anion exchanger containing ~7% of rhodium (Rh : N = 1 : 3.4), we studied [59] the dependence of the rate of hydrogen evolution on the size of the granules and on the concentration of the catalyst and of the two reactants (H^+ and V^{2+}(aq) ions). At high enough rates of stirring of the solution, the rate of evolution of hydrogen was found to increase in proportion to the amount of catalyst (i.e. α was independent of the amount of catalyst). Thus the rate of hydrogen evolution is limited under these conditions by processes involving the catalyst, and not by mass transfer in solution or at the interface between the solution and the gas phase. However, we found a substantial increase in rate for a decrease in the particle size of the catalyst (for example, α = 8.7 for granules 2 mm in diameter and α = 640 for the same catalyst ground to a granule size of less than 0.1 mm, see Nos.13 and 14 in Table 1). This suggests rate limitation by mass transfer processes within the polymer granule rather than by the catalytic reaction.

A study [59] of the dependence of α on the concentration of V^{2+}(aq) showed an increase of α with $[V^{2+}(aq)]$ at low concentrations of V^{2+}(aq) (<5×10^{-3} M), but at higher concentrations (5×10^{-3}–2×10^{-2} M) α was independent of $[V^{2+}(aq)]$. It follows that at low concentrations of V^{2+}(aq) the process is limited by reactions involving these ions. On the other hand at high concentrations of V^{2+}(aq) the rate of this step is so high that the reaction is no longer rate-limiting. Thus the diffusion within the polymer particle of some other participant in the reaction (reactant, or product) becomes rate-limiting at these concentrations.

The dependence of α on the concentration of H^+ ions was studied only at low concentrations of V^{2+}(aq) in solutions of constant ionic strength (μ = 2 M) generated by additions of sodium sulphate: in this case the changes in α are described by the equation $\alpha \propto [H^+]^{0.2}$. The data were obtained by measuring α at different pH values for the same sample of catalyst previously activated at pH 2 and 298 K in a solution containing 10^{-2} M VSO_4 and a ratio of $[V^{2+}(aq)]/[Rh^{3+}] = 20$. Thus in this case the dependence of α on $[H^+]$ is weaker than expected from the law of mass action if the rate-limiting step involves H^+. As in the case of the monomer catalyst, further work is needed to explain the observed dependence of α on $[H^+]$ for this catalyst. However, we note that in this case the dependence could reflect the influence of H^+ ions on the structure of the polymer granule, which contains easily protonised nitrogen atoms.

It follows that at high concentrations of V^{2+}(aq) the rate of the catalytic process with rhodium catalysts in anion exchange resins is determined (most probably) by diffusion of the products of reaction (3) within the polymer granules, i.e. by the diffusion of V^{3+} cations up or of hydrogen molecules.

As expected, all these rhodium catalysts remain active when used in the classical photocatalytic system for hydrogen evolution from water with the *tris*-bipyridyl complex of ruthenium(II) (photocatalyst), methylviologen MV^{2+} (intermediate electron-transfer acceptor), and anions of ethylenediaminetetra-acetic acid $EDTA^{2-}$ (irreversibly consumed electron donor):



Throughout this review we shall use the symbol $EDTA^{2-}_{ox}$ to denote the products of irreversible oxidation of $EDTA^{2-}$.

Polymer rhodium catalysts (like other catalysts containing finely divided metals when activated) cause fairly rapid deactivation of this photocatalytic system, probably by hydrogenating the charge transfer agent MV^{2+}.

It is interesting to compare the activity of these catalysts in the evolution of hydrogen from aqueous solutions with the activity of the hydrogenase enzymes in the same reaction.

Published values of α for hydrogenase lie between 10^4 and 10^7 mole H_2 mole^{-1} of enzyme h^{-1},[48] i.e. they are much greater than the α values for catalysts based on rhodium polymer complexes. The difference becomes much smaller if we compare the α′ activities, i.e. the activities referred to unit mass of rhodium and of the enzyme (rather than to 1 mole of rhodium and of the enzyme). Thus for the more active catalysts based on an anion exchanger α′ can be as high as ~0.5 mole H_2 g^{-1} of catalyst h^{-1}, as compared with 0.2–200 mole H_2 g^{-1} of enzyme h^{-1} for hydrogenase[48].

While inferior to the best hydrogenases in catalytic activity per unit weight, the catalysts based on rhodium polymer complexes are superior in stability, especially in acid media (where hydrogenases are deactivated almost instantaneously). Furthermore, unlike hydrogenase, the activated catalysts based on anion exchangers and on PEI can be stored in air for long periods without significant loss of activity. We also note that the activity of rhodium polymer catalysts can be improved by eliminating (or decreasing) the diffusional limitations of the reaction.

Catalytic activity towards the evolution of hydrogen from water under the influence of one-electron reducing agents was observed also for the complexes of PEI with ruthenium[57], palladium, and platinum[60]. Thus catalysts for the evolution of hydrogen from water can be obtained by immobilising ions of other metals (not only rhodium) on PEI and reducing them to the metal. An important practical advantage of this type of catalyst for the future is their stability in aqueous solutions over a very wide range of pH, and their availability in the form of granules or films with controlled geometric characteristics.

2. Systems with Heteropoly Compounds

The heteropoly compounds have been identified as a potentially useful class for use in systems for evolution of hydrogen from water: as was pointed out above, they can be treated as models of the active centres in hydrogenases and nitrogenase. We know, for example, that highly reduced forms of heteropolyacids (HPA) of the 12-series have negative (or near-zero) electrochemical reduction potentials relative to the NHE, i.e. they satisfy the thermodynamic requirements for hydrogen evolution from acidic aqueous solutions. Thus the reduction potential E_0 for the acid $H_3[PMo_{12}O_{40}]$ (HPA-I) reduced by six electrons and for the acid $H_4[SiMo_{12}O_{40}]$ (HPA-II) reduced by four electrons is close to +0.1 V, whereas for the heteropolyacids reduced by two electrons $H_3[PW_{12}O_{40}]$ (HPA-III) and $H_4[SiW_{12}O_{40}]$ (HPA-IV) the E_0 values are close to 0 and −0.2 V respectively[61–63]. We have observed[64,65] spontaneous and relatively fast hydrogen evolution from acid solutions by these reduced forms of the heteropolyacids, without any auxiliary catalysts.

The reaction has been studied most fully for solutions of HPA-IV (silicotungstic acid),[64,66] whose structure is shown in Fig.5. It was found that HPA-IV reduced by two electrons on zinc amalgam (HPA.H_2) can evolve hydrogen rapidly from aqueous solutions in a yield of almost 100% of stoichiometric for the reaction

$$\mathrm{HPA\cdot H_2} \xrightarrow{k_{eff}} \mathrm{HPA\cdot H^{+1}/_2H_2\uparrow} \ . \qquad (4)$$

The kinetics of this process satisfy the scheme

$$\mathrm{HPA.H_2} \xrightarrow{k_1} \mathrm{HPA + H_2\ (slow\ H_2\ evolution)} \ , \qquad (4a)$$

$$\mathrm{HPA.H_2 + HPA \rightarrow 2HPA.H\ (fast\ disproportionation)} \ , \qquad (4b)$$

which corresponds to a first-order equation for the change in concentration of the reactants in the overall reaction. In this scheme HPA and HPA.H are, respectively, the initial (oxidised) form of the acid and the form reduced by two electrons (HPA-IV). The rate constant k_1, measured in three independent experiments from the disappearance of HPA.H_2 (monitored by an optical method) and from the accumulation of H_2 (monitored chromatographically) or of HPA.H (monitored by ESR), was found to be $k_1 = (3.5 \pm 2) \times 10^{-4}$ s^{-1}. (The k_1 value given here is a slight improvement over the previously reported value[64] $k_1 = k_{eff}/2 = (6 \pm 4) \times 10^{-4}$ s^{-1}.)

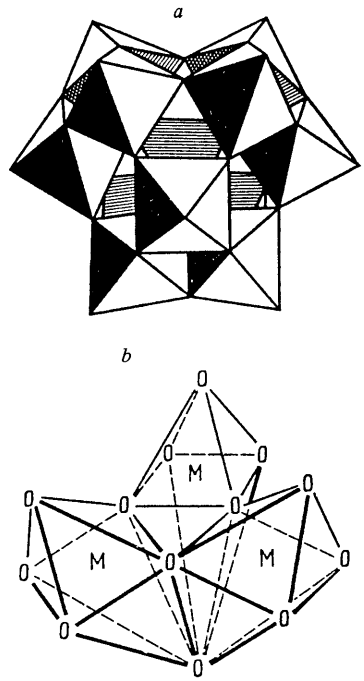


Figure 5. (*a*) Typical structure of heteropoly anions of the 12-series. The metal cations M are within the corner- and edge-sharing octahedra formed by the oxygen anions, the hetero-atom lies at the centre of the heteropoly anion; (*b*) configuration of the ions in a "triad" of adjacent octahedra.

The k_1 values obtained from the disappearance of HPA.H_2 and from the accumulation of H_2 are shown, as an example, in Fig.6. The fast disproportionation step (4b) is further confirmed by the lower yield of H_2 caused by the addition of the oxidised form to the solution, while the constant k_1 for the H_2 evolution process is unchanged.

It was found[66] that the hydrogen evolution rate constant k_1 is almost independent of pH in the range pH 1–4. This means that the protonation of the HPA forms reduced by one or two electrons cannot be rate-limiting, and we may assume that the step which controls the rate of evolution is the reduction of the strongly bound ("isolated") protons, previously observed[67] by NMR in the crystal hydrates of the reduced forms of some HPA, or the reduction of water molecules solvating the HPA.H_2 species. The mechanism of this reaction has not yet been fully investigated, but a number of significant features can already be pointed out. Thus we have found[66] a marked isotope effect, giving an almost two-fold decrease in reaction rate between ordinary water and

heavy water. The isotope effect confirms that the rate-limiting step of reaction (4) involves protons or water molecules. We also found that the reaction has a low activation energy $E^{\neq} = 6 \pm 3$ kcal mole^{-1} but a high and negative entropy of activation $\Delta S^{\neq} \cong -50$ e.u. The large value of $|\Delta S^{\neq}|$ can be explained, for example, by the complexity of the elementary act (reduction of internal protons with transfer of two electrons from the HPA.H_2 skeleton to two bound protons already in close proximity and ready to form an H_2 molecule). We also note that this reaction is markedly accelerated by visible (including red) light, which assists the transfer of electrons from the HPA.H_2 skeleton to protons or water molecules attached to the skeleton by exciting the inter-valency charge transfer levels of the reduced forms of HPA.[62,68]

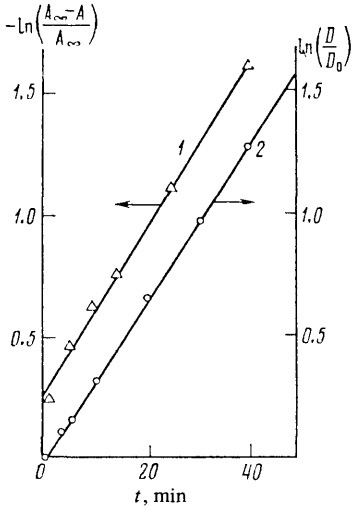


Figure 6. Kinetics of the hydrogen evolution (*1*) and of the disappearance of HPA.H_2 (*2*) in aqueous solutions of reduced 12-silicotungstic heteropolyacid (HPA-IV) at pH 2 and room temperature under anaerobic conditions: A is the height of the hydrogen peak in the chromatogram, A_∞ defines the total hydrogen evolution (initial concentration of heteropolyacid 2.2×10^{-3} M); D is the optical density of the solution at $\lambda = 650$ nm for an optical path 1 cm long, D_0 refers to the initial instant (initial concentration of heteropolyacid 5×10^{-4} M).

Hydrogen evolution has been observed also from aqueous-alcoholic solutions (0.1–10 M in alcohol) of phosphomolybdic acid reduced by six electrons (HPA-I), silicomolybdic acid reduced by four electrons (HPA-II), and phosphotungstic acid reduced by two electrons (HPA-III).[65] The rate constants ($k_1 \cong 10^{-4}$–10^{-3} s^{-1}) for all these HPA were close to the value $k_1 = (3.5 \pm 2) \times 10^{-4}$ s^{-1} given above for HPA-IV in aqueous solution. Hence we can assume that the evolution reaction has the same rate-limiting step for any highly reduced form of these heteropolyacids.

The ability of the reduced forms of HPA to evolve hydrogen from aqueous solutions, coupled with the well known tendency of HPA to be reduced by various types of reducing agents, suggest that HPA may act as homogeneous catalysts for the evolution of hydrogen from water by various reducing agents.

In fact, HPA-I and HPA-II catalyse the evolution of hydrogen from acidic aqueous solutions of several two-electron reducers, including relatively weak ones such as tin(II) ($E_0 = 0.15$ V relative to the NHE) or the sulphite ion SO_3^{2-} ($E_0 \cong 0.07$ V). We note that in the presence of these reducing agents the formation of highly reduced forms of HPA-I and HPA-II was not observed, and the rate of evolution of H_2 was much lower than the rate of evolution from highly reduced forms of HPA under otherwise similar conditions. Hence we may assume that the observed slow evolution of hydrogen (over tens of hours) is due either to the very weakly reduced forms of HPA-I and HPA-II themselves (for example, by the reaction HPA.H + HPA.H → 2HPA + H_2, which can go from left to right at low H_2 pressures) or to the disproportionation of these forms to give more highly reduced heteropolyacids, which can evolve hydrogen (as we shall show below) with fairly high rate constants.

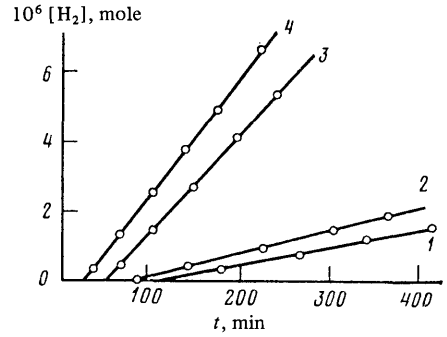


Figure 7. Kinetics of hydrogen evolution from 8 cm^3 of an 8.7 M solution of ethanol in water containing 0.25 M H_2SO_4 and: *1*) 1.3×10^{-4} M HPA-I, *2*) 10^{-4} M HPA-II, *3*) 5×10^{-4} M HPA-III, *4*) 4×10^{-4} M HPV-IV, irradiated with filtered u.v. light ($\lambda < 400$ nm) from a DRSh-1000 lamp.[65]

Heteropolyacids can also act as photocatalysts and bring about (under the influence of light) endoergic ($\Delta G > 0$) reactions in which hydrogen is evolved from water as a result of the irreversible removal of donors. Thus we have observed[65] hydrogen evolution by irradiation of oxidised forms of heteropolyacids in aqueous-ethanolic (0.1–10 M in alcohol) solutions at pH 1–4 with near u.v. light. Typical kinetic curves for this process are shown in Fig.7. We note that hydrogen evolution begins after a period of induction, and then proceeds at a constant rate. The rate of evolution stays constant even after lengthy irradiation, when the number of moles of H_2 evolved is much greater than the number of moles of HPA present in the irradiated solution.

Thus the hydrogen evolution process is truly catalytic. From the absorption spectra in the visible and u.v. regions and from fast redox titrations with $KMnO_4$ solutions we find that under the influence of light of wave length $\lambda \leq 400$ nm, HPA-I is reduced by two, four, and six electrons successively during the induction period, HPA-II by two and four electrons, and HPA-III and HPA-IV by one and two electrons. The quantum yield of the formation of reduced forms of HPA in the initial portions of the kinetic curves of Fig.7 (at $\lambda = 333$ nm) is several per cent for HPA-I and HPA-II and ~20% for HPA-III and HPA-IV.[65,69] Hence the induction

period of the H_2 evolution kinetic curves seems to be related to the accumulation of forms of HPA which are reduced sufficiently to evolve hydrogen spontaneously from acid aqueous-ethanolic solutions. These reduced forms of HPA are produced by the oxidation of ethanol. The detection[65] of acetaldehyde (in a proportion of 1 : 1 with the evolved hydrogen) after the photocatalytic reaction is consistent with this conclusion.

A decrease by a large factor in the intensity of u.v. light causes a substantial increase in the period of induction, though the rate of evolution of H_2 on the linear part of the curve is only marginally affected. The generation of hydrogen continues even after the light is switched off: we observe only a gradual slowing down as the reduced form of the HPA is used up[65].

For aqueous-ethanolic solutions of silicotungstic acid (HPA-IV) a rate constant of $k_1 \cong 5 \times 10^{-4}$ s^{-1} was calculated for the evolution of hydrogen on the stationary part of the accumulation curve (Fig.7). The constant was defined as the ratio of the rate of evolution of H_2 to the steady-state concentration of the two-electron reduced form HPA.H_2 of this heteropolyacid (see above).

These facts suggest the following overall scheme (for HPA-III and HPA-IV, say) to describe the photocatalytic evolution of H_2 from aqueous-ethanolic solutions of the oxidised forms of heteropolyacids:

$$C_2H_5OH + HPA \xrightarrow{h\nu} CH_3CHO + HPA \cdot H_2 \qquad (5a)$$

$$HPA \cdot H_2 \longrightarrow HPA + H_2\uparrow \cdot \qquad (5b)$$

The rate-limiting step is reaction (5b), which takes place spontaneously even in the absence of light but (as was pointed out above) can be accelerated by irradiation with visible light of wavelength corresponding to the intervalency charge transfer absorption band. Unlike reaction (5b), reaction (5a) proceeds only under irradiation. It is almost certainly a complex reaction, i.e. a reaction consisting of several steps[69]. Further work is needed to clarify the relative roles of two-electron processes

$$C_2H_5OH + HPA \xrightarrow{h\nu} CH_3CHO + HPA \cdot H_2$$

and of one-electron processes

$$C_2H_5OH + HPA \xrightarrow{h\nu} CH_3\dot{C}HOH + HPA{\cdot}H$$

$$C_2H_5OH + HPA{\cdot}H \xrightarrow{h\nu} CH_3\dot{C}HOH + HPA \cdot H_2$$

$$CH_3\dot{C}HOH + HPA \rightarrow CH_3CHO + HPA{\cdot}H$$

$$CH_3\dot{C}HOH + HPA{\cdot}H \rightarrow CH_3CHO + HPA{\cdot}H_2,\ HPA + HPA{\cdot}H_2 \rightleftarrows 2HPA{\cdot}H$$

in reaction (5a).

Thus in this photochemical process the heteropolyacids take part in cyclic reactions including steps in which the HPA are reduced by two or more electrons, followed by hydrogen evolution by the reduced forms of HPA and by regeneration of the initial (oxidised) forms. Under these conditions the HPA performs two functions at the same time: that of a photo-catalyst and that of a catalyst for the "dark" H_2 evolution reaction. The photo-catalytic hydrogen evolution

$$C_2H_5OH \xrightarrow[PC]{h\nu} CH_3CHO + H_2\uparrow$$

in this system is an endoergic process, leading to a small (~0.2 eV) acquisition of energy from the light at each act of evolution of molecular H_2.

III. EVOLUTION OF OXYGEN FROM WATER

This step is much more difficult than the hydrogen evolution to carry out in practice, because reaction (2) requires the transfer of four electrons, and furthermore conditions leading to the formation of the product molecule (oxygen) in the triplet rather than the singlet state must be provided. A systematic search for catalysts for reaction (2) has only recently been started. We have examined[70–73] a series of homogeneous metal complex catalysts for reaction (2), using the compounds $Ru(bipy)_3^{3+}$, $Fe(bipy)_3^{3+}$, and $Fe(phen)_3^{3+}$ as the oxidiser D^+. Some of these catalysts allow oxygen evolution from water not only in alkaline or neutral solutions but also in weakly acid solutions (down to pH 5). The series of homogeneous catalysts for the oxygen evolution step was also reported from another laboratory almost simultaneously[74–77]. Many heterogeneous catalysts for this step have also been discovered[21,52,75–87]: for example, the oxides of ruthenium, platinum, iridium, cobalt, and manganese.

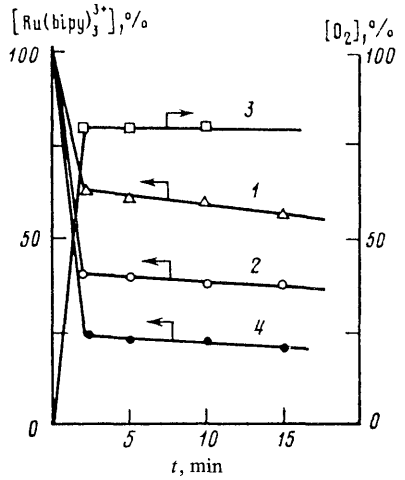


Figure 8. Kinetics of the reduction of the oxidiser and of the formation of oxygen during fast adjustment to a more alkaline pH of 8×10^{-4} M solutions of $Ru(bipy)_3^{3+}$ in 0.01 *N* HCl: *1*) and *4*) adjusted to a final pH of 3.5 and 6 respectively in the absence of the catalyst, *2*) and *3*) adjusted to a final pH of 3.5 in the presence of the catalyst (5×10^{-5} M $CoCl_2$), temperature 298 K. The stoichiometry of the oxygen evolution was calculated with respect to the reduced fraction of the oxidiser[73].

1. Systems with Homogeneous Catalysts Based on Transition Metal Complexes

We have studied two classes of compounds which act as homogeneous catalysts for reaction (2): 1) the partially hydrolysable (or aquated) complexes of various transition metals with nitrogen- or oxygen-containing ligands[70,71,73] (see also Ref. 76), and 2) water-soluble phthalocyanines and porphyrins of various metals[72]. Catalysts of the first type are the more effective, the highest activity (up to one molecule of O_2 per metal atom in the catalyst per minute at 20 °C) being found in the iron, cobalt, and copper complexes, but they are less stable than the catalysts of the second type.

It has been reported[75–77,79,84] that compounds of the first type have a high catalytic activity not only for the "dark" evolution of oxygen from water but also in model photo-catalytic systems, in which the evolution of oxygen from water is coupled with the irreversible reduction of an electron acceptor.

The study of the mechanisms by which the homogeneous catalysts contribute to reaction (2) is still in progress, but some important features of their mode of action have already been established. We should stress first of all the experimental difficulties encountered in the study of reaction (2). When complexes with bipy or phen are used as the oxidiser D^+ the reaction is very sensitive to effects of the wall of the vessel. For example, in glass reactors oxygen is sometimes evolved by reaction (2) even in the absence of special catalysts, the amount of oxygen evolved depending on the composition of the glass and on the presence of rough areas or micro-cracks on its surface. The requirement of wall inertness is most fully met by polyethylene vessels.

Another difficulty in the study of the mechanism of action of these catalysts in reaction (2) is the lack of sufficiently fast methods of recording the kinetics of oxygen evolution. The characteristic times of the fast step in reaction (2) in the presence of the catalyst and after pH adjustment to the required alkalinity are usually a few seconds (see below, and Fig.8). However, the time constant of the fastest instrumental methods of detecting oxygen directly in solution (by using a Clark electrode) is 20–30 s. Therefore the most informative data on the kinetics of oxygen evolution (i.e. directly from the activity of the catalyst) are not available to us at the moment. The effectivness of the catalyst can only be characterised by the ratio of the amount of oxygen evolved to the amount expected from stoichiometry considerations. This ratio (β), expressed in per cent, will be termed the effectiveness of the catalyst.

It is found that 100% effectivness is only very rarely achieved in a catalyst: a much lower β value is usually obtained. This is probably due to the partial loss of oxidiser (D^+) by fast oxidation side-reactions involving the ligands (which enter into the composition of both the oxidisers and the catalysts). We note that side reactions in the absence of the catalyst can cause substantial reduction of D^+ in less than 10 s (~40% in acid solutions and ~90–95% in alkaline solutions, see below and Fig.8): no oxygen is evolved in this case. Thus the role of the catalyst in reaction (2) is to guide the reduction of D^+ towards the evolution of oxygen rather than towards the oxidation of the ligands.

In the presence of catalysts, after adding alkali to obtain the required pH to the acid (pH 1–2) solutions containing the initial reagents (oxidiser and catalyst) as in the experiments[70–72] on the initiation of the oxygen evolution, only a part of the oxidiser is consumed in the fast (a few seconds) oxygen evolution and ligand oxidation processes (see Fig.8). The unused oxidiser D^+ is reduced more slowly, in times of the order of tens of minutes. With some (but not all) catalysts this slow reduction of the oxidiser is accompanied by evolution of oxygen from the water by reaction (2).

The loss of oxidiser in the fast step of the process is strongly dependent on the pH of the solution. Thus if alkali is added to give pH 3 approximately one-half of the oxidiser is usually reduced rapidly; at pH 9 this loss amounts to 80–90%.

It is interesting to find that the effectiveness β measured at pH 3 for most of the homogeneous catalysts under the most favourable conditions and referred to the amount of oxidiser reduced in the fast reactions does not vary over a wide range (see Table 2). We should also note the complex behaviour of some of these homogeneous catalysts in solutions with different pH. Thus, whereas at pH 3 all the cobalt complexes have approximately the same effectiveness as catalysts when $Ru(bipy)_3^{3+}$ is used as the oxidiser (see Table 2), in solutions of pH 9–10 they can be arranged in the following series of increasing effectiveness:

$$\underset{\beta,\ \%}{\text{Catalyst}}\ \underset{10}{Co(NH_3)_6^{3+}} < \underset{39}{Co(NH_3)_5Cl^{2+}} < \underset{42}{Co(NH_3)_5(H_2O)^{3+}} < \underset{60}{Co^{2+}(aq)} < \underset{66}{Co(NH_3)_4(H_2O)_2^{3+}} < \underset{70}{Co(bipy)_{3-x}(H_2O)_x^{3+}}$$

This series probably reflects the role of the coordination of water molecules or hydroxyl ions to the catalyst molecules in the evolution of oxygen molecules under these conditions.

Table 2. Consumption of oxidiser (Q) in the fast step of the water oxidation process and effectiveness β of various homogeneous catalysts in an 8×10^{-4} M solution of $Ru(bipy)_3^{3+}$ after pH adjustment to pH 3.0–3.2 at 298 K (c is the concentration of catalyst) [73].

$10^4 c$, M	Q, %	β, %	$10^4 c$, M	Q, %	β, %
0	40	0	$[Co(NH_3)_5(H_2O)]Cl_3$		
$CoCl_2$			0.9	30	45
0.5	60	85	8.3	55	85
2.2	55	75	30.0	55	85
4.3	30	65	$[Co(NH_3)_4(H_2O)_2]Cl_3$		
6.4	20	27	2.0	50	70
Cis- and *trans*-$[Co(en)_2Cl_2]Cl$, *trans*-$[Co(en)_2Cl(H_2O)]Cl_2$			20.0	40	70
0.5	60	80	Tetrasulphophthalocyanine of cobalt(II)		
2.2	60	75	0.07	55	70
8.3	60	75	0.22	60	60
20.0	45	70	0.64	65	40
$[Co(NH_3)_5Cl]Cl_2$			$[(bipy)_2FeOFe(bipy)_2]Cl_4$		
5.0	50	80	0.25	60	85
10.0	50	80	1.0	60	85
			10.0	50	90

Note. The precision of the determination of Q and β is ±5%.

The complexity of the homogeneous catalysis process combining the above catalysts with *tris*-bipyridyl and *tris*-phenanthroline complexes as oxidisers is confirmed by the strong dependence of β on the experimental conditions, in particular the pH and the storage time of the solutions before the reaction, and also on the procedure used in mixing the reagents (for example, whether the catalyst is added to the acid solution of oxidiser before adding alkali, or whether the catalyst is added in an already alkaline solution to an acid solution of the oxidiser). Evidently these results can be explained by postulating hydrolysis processes in the activation of the catalyst: of course, both the rate and the direction of these processes can be expected to depend on the pH of the medium.

The role of hydrolysis in the conversion of the initial complexes into catalytically active compounds has been demonstrated for systems containing the complexes $Fe_m(bipy)_n \cdot (OH)_p^{(3m-p)+}$ or $Fe_m(phen)_n(OH)_p^{(3m-p)+}$ at pH > 4 as catalysts[70]. It was shown that the bipyridyl and phenanthroline complexes of iron(III) containing OH^- ions as ligands are much more effective catalysts than the same complexes without the OH^- ligands. By comparing the data on the

effectiveness of these complexes with the data on their hydrolysis mechanism we conclude that in some of our systems the catalytically active intermediates are binuclear di-μ-hydroxo $\left(M\begin{smallmatrix}OH\\OH\end{smallmatrix}M\right)$ or di-μ-oxo $\left(M\begin{smallmatrix}O\\O\end{smallmatrix}M\right)$ structures (where M is a metal).

Evidently, the oxygen evolution reaction begins with a series of four consecutive one-electron reactions in which the catalyst is oxidised by D^+ particles, and each metal ion in the binuclear catalyst can give up two electrons to the oxidisers. The subsequent reactions (oxygen evolution and regeneration of the active forms of the catalyst) proceed without the formation of free (non-coordinated) forms of intermediates in the oxidation of water such as ·OH radicals and also, at least for some of the present catalysts, H_2O_2 molecules and $H\dot{O}_2$ radicals[70]. For example, the catalytic action of partially hydrolysed bipyridyl complexes of iron(III) can be interpreted by the following alternative schemes:

$$M\begin{smallmatrix}OH\\OH\end{smallmatrix}M + 2D^+ \rightarrow M\begin{smallmatrix}O\\O\end{smallmatrix}M + 2H^+ + 2D$$

$$M\begin{smallmatrix}O\\O\end{smallmatrix}M + 2D^+ \xrightarrow{2H_2O} M\begin{smallmatrix}OH\\OH\end{smallmatrix}M + 2H^+ + 2D + O_2\uparrow \qquad (6)$$

or

$$M\begin{smallmatrix}OH\\OH\end{smallmatrix}M + 2D^+ \xrightarrow{2H_2O} M_2(H_2O)_2 \text{ (or } 2M(H_2O)) + 2H^+ + 2D + O_2\uparrow \qquad (7)$$

$$M_2(H_2O)_2 \text{ (or } 2M(H_2O)) + 2D^+ \rightarrow M\begin{smallmatrix}OH\\OH\end{smallmatrix}M + 2H^+ + 2D$$

For the catalysts in which M = Fe(III) or Co(III) the evolution of molecular oxygen from an oxidised $M\begin{smallmatrix}OH\\OH\end{smallmatrix}M$ centre can take place through the formation and dissociation of a binuclear μ-peroxo complex

$$M - O_2^{2-} - M \rightleftarrows 2M^- + O_2\uparrow$$

or a mononuclear peroxo complex

$$M - O_2^- \rightleftarrows M - O_2 \rightleftarrows M^- + O_2\uparrow$$

as intermediates. These reversible oxygenation reactions of cobalt(II) and iron(II) complexes in alkaline solutions are well known (see, for example, Refs.88–91).

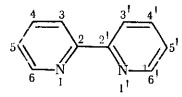
Among the catalysts of the second type the most effective (β ≅ 70%) are the tetrasulphophthalocyanine and tetrasulphophenylporphin of cobalt(II).[72] If $Ru(bipy)_3^{3+}$ is used as the oxidiser D^+ the effectiveness of the tetrasulphophthalocyanines of various metals at pH 9 can be arranged in the following sequence:

Metals	Co(II)	> Fe(II)	> Zn II	> Cu(II)	> Ni(II)	> Mn(II)	> Cr(II)
β, %	65	47	25	21	18	14	5

Metal-free phthalocyanines do not show a significant catalytic activity. The mechanism of the action of these catalysts is still unclear. We can note, nevertheless, that the catalytic activity of metal phthalocyanines is not produced by dissociation with formation of aquo-complexes of the metal ions. Thus, at ~10^{-5} M concentration the aquo-ions of Cr(III), Mn(II), Bi(II), and Al(III) have no catalytic activity towards the oxidation of water by oxidisers of the $Ru(bipy)_3^{3+}$ type, whereas the phthalocyanines of the same metals at the same concentration have a marked catalytic activity[72]. We should also stress that in very acid solutions (in which the reaction (2) is suppressed) some of these metal phthalocyanines undergo a fast and quantitative two-electron oxidation accompanied by one-electron reduction of the oxidiser $Ru(bipy)_3^{3+}$. It is at least possible that in more alkaline solutions these doubly oxidised forms of metal phthalocyanines take part (as intermediates) in the oxygen evolution reaction.

An interesting feature of these catalysts, providing additional evidence of the complexity of the catalytic reaction (2), is the presence at pH > 4 of clear maxima in the plots of the effectiveness of the catalyst against concentration. For example, at pH 9 the optimum concentration for catalysts of the first group is ~10^{-4} M, and for catalysts of the second group ~10^{-5} M. The existence of optimum concentrations of the homogeneous catalysts is noted also for the evolution of oxygen at pH 3 (see Table 2), but in this case the dependence of β on the concentration of the catalyst is usually monotonic, without extrema.

The possibility that the role of the oxidisers D^+ in reaction (2) goes beyond the transfer of an electron from the catalyst to the oxidiser cannot be excluded. Indeed, the addition of anions (chloride, perchlorate, sulphate, carbonate, acetate, borate, etc.) as sodium salts partially suppresses both the evolution of oxygen in reaction (2) and the secondary reduction of D^+ by the oxidation of the ligands (even in the absence of catalysts). However, the catalyst effectiveness β calculated from the amount of oxidiser D^+ which is reduced does not vary significantly under these conditions. We are therefore forced to the conclusion that reaction (2) and the secondary reaction share a number of steps which are affected by the interaction between the particular oxidised (D^+) used in these experiments and the anions, but are unaffected by the catalyst. Thus, in the proton magnetic resonance spectra of the complex $Ru(bipy)_3^{3+}$ a strong chemical shift of the signals from the 6 and 6′ protons of bipyridyl



is observed after addition of various anions (see Fig.9), due no doubt to the out-of-sphere coordination of the anions to the bipyridyl ligand. This anion coordination may also suppress some other interaction of the oxidiser with water molecules (or their ionic forms) playing an as yet unrecognised role in both reaction (2) and the secondary process. Work on these effects is in progress.

At the same time the inner-sphere coordination of water to the cation of the oxidiser by replacing even one of the coordinating nitrogen atoms of the ligands does not appear to be an intermediate step of reaction (2). Thus we have shown[73] that the mixed complexes of ruthenium(III) $[Ru(bipy)_2(Py)_2]^{3+}$ (where Py is pyridine), in which the replacement of the ligands probably occurs at different rates and with different equilibrium constants than for the *tris*-bipyridyl complex, can evolve oxygen from water with the same effectiveness as $Ru(bipy)_3^{3+}$ when used as the oxidiser D^+ in the presence of homogeneous catalysts[73]. However, in the complexes $[Ru(bipy)_2.(Py)(H_2O)]^{3+}$, which contain water in the first coordination sphere, this property is not found because their oxidation potential is too low. We note that the even more highly hydrolysed form of this complex $[RuO(bipy)_2]^{2+}$, though itself unable to oxidise water, is nevertheless an effective homogeneous catalyst for the oxidation of water when $Ru(bipy)_3^{3+}$ is used as the oxidiser D^+ [73] (see also Refs. 92 and 93).

We may hope that work now in progress on the mechanism of the homogeneous catalysis of reaction (2) by using $Ru(bipy)_3^{3+}$ as the oxidiser will lead to the development of effective and stable catalysts for the oxygen evolution step, able to operate in a closed water decomposition cycle using the $Ru(bipy)_3^{2+}$ comples as the photocatalyst for step (1).

2. Systems with Heterogeneous Catalysts Based on the Hydroxides and Mixed Oxides of the Transition Metals

The search for and study of potential heterogeneous (as well as homogeneous) catalysts for reaction (2) is an important current problem. As was mentioned above, these catalysts are being studied in a number of laboratories, the materials in most cases being simple oxides. We have examined[94] the possibility of using another class of compounds as heterogeneous catalysts of reaction (2): base metal hydroxides and spinels, which are mixed oxides of general formula $M^{II}M^{III}_2O_4$ (where M^{II} and M^{III} are bivalent and a tervalent metal respectively). Spinels of various compositions are widely used as oxidation catalysts and as anodes for the electrochemical evolution of oxygen[95].

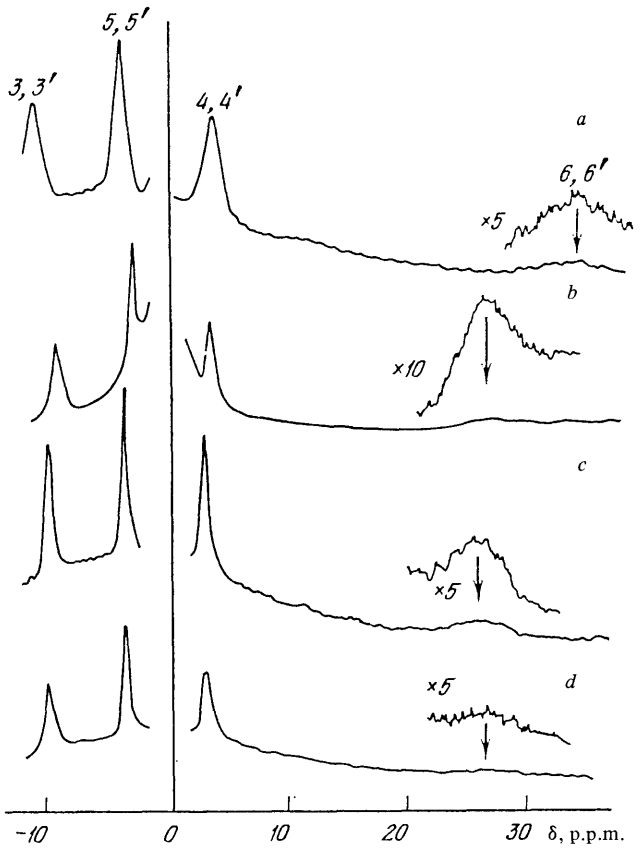


Figure 9. NMR spectra ("Bruker CXP-300" Fourier spectrometer, frequency 300 MHz) of a 10^{-3} M solution of $Ru(bipy)^{3+}_3$ in D_2O containing also: (*a*) 0.01 M DCl, (*b*) 1 M DCl, (*c*) 1 M NaCl, (*d*) 1 M Na_2SO_4; temperature 293 K, 200 spectral scans. The chemical shifts are measured relative to the signals of the water protons. The peaks are numbered according to the position of the protons in 2,2′-bipyridyl.

Measurements of the effectiveness β of heterogeneous catalysts (hydroxides and spinels) used in conjunction with *tris*-bipyridyl complexes of ruthenium(III) and iron(III) as the oxidiser D^+ are summarised in Table 3. As in the study of the homogeneous catalysts, the amount of oxygen evolved was determined after adding a 0.1 *N* solution of NaOH to weakly acid (pH ~ 2, spinels) or to neutral solutions (hydroxides) of the oxidiser containing the catalyst. The weight of catalyst added was 20 mg for 10 ml of solution; no oxygen was evolved unless the solution was made alkaline.

We should stress that spinels prepared by standard methods may contain various impurities such as the salts used in their preparation or oxides or hydroxides foreign to the spinel. Most of these impurities are removed by steeping the spinel in a weakly acid solution, but this treatment transfers to the solution metal ions which can act (as stated above) as homogeneous catalysts for reaction (2) even at very low concentrations (10^{-4}–10^{-5} M). Therefore all the spinel samples were finely ground before the determination of β and washed repeatedly with 0.1 *N* hydrochloric acid until free from metal ions, thus ensuring the absence of effects from homogeneous side-reaction on the measurements.

Table 3. Effectiveness β of heterogeneous catalysts in 8×10^{-4} M solutions of $Ru(bipy)^{3+}_3$ and $Fe(bipy)^{3+}_3$ at 298 K.

Catalyst	β %	Catalyst	β %
Oxidiser $Fe(bipy)_3^{3+}$		Oxidiser $Ru(bipy)_3^{3+}$	
$NiCo_2O_4 \cdot Co_2O_4$	70	$CoFe_2O_4$	60
$CuCr_2O_4 \cdot CoCr_2O_4$	50	$CoFe_2O_4$*	60
$CoFe_2O_4$	40	$CoFe_2O_4$**	17
$FeCr_2O_4$	40	$Co^{II}Co_2^{III}O_4$	35
$Co^{II}Co_2^{III}O_4$	37	$Cr_2(OH)_3$	60
$CoCr_2O_4$	35	$Cu(OH)_2$	45
		$Fe(OH)_3$	40
		$Co(OH)_3$	25
		$Ni(OH)_3$	20
		$Al(OH)_3$	0

*pH 5–6; **pH 3–4, otherwise pH 10–11.

Note. The precision of the measurement of β is ±5%. The catalyst was ground to a powder of particle size less than 0.05 mm and was taken in amounts of 20 mg per 10 cm^3 of solution.

The catalytic activity of the iron(III) and cobalt(III) hydroxides in reaction (2) is mentioned also in Ref.76.

The heterogeneous catalysts studied in our laboratory are similar to the homogeneous catalysts in effectiveness (see Tables 2 and 3), but their stability is much higher. In addition to the substances listed in Table 3, zinc and copper ferrites and iron and copper cobaltites have been found to be catalytically active in reaction (2).

It would be premature to attempt a discussion of the mechanism of the oxidation of water by reaction (2) in the presence of spinels. In particular, the effect of the spinel structure and of the nature of the bivalent and tervalent metal cations is still unclear. It is obvious, however, that surface compounds containing water or its fragments must play an important part in reaction (2). In contact with water the spinel surface may become rapdily hydroxylated, so that the catalytically active centres are not the spinels themselves but compounds not very different from the hydroxides of the corresponding metals. In this case we would expect the formation on the catalyst surface of bridging compounds similar to the complexes proposed for reactions (6) and (7).

IV. PHOTOCHEMICAL CHARGE SEPARATION

The lack of effective methods of realising reaction (2) in practice is the most serious obstacle to the development of molecular photocatalytic systems for the decomposition of water in a closed cycle (i.e. a cycle in which no substance is consumed irreversibly except water). The main problem is to suppress the reverse recombination reaction $D^+ + A^- \rightarrow D + A$, which is a simple exothermic process and therefore usually much faster than the complex catalytic reactions (2) and (3).

Several possible ways of suppressing the reverse reaction are being studied in our laboratory at present. Two of these will be discussed below: one based on the use of lipid vesicles, the other on micro-emulsions.

1. Charge Separation in Solutions of Lipid Vesicles

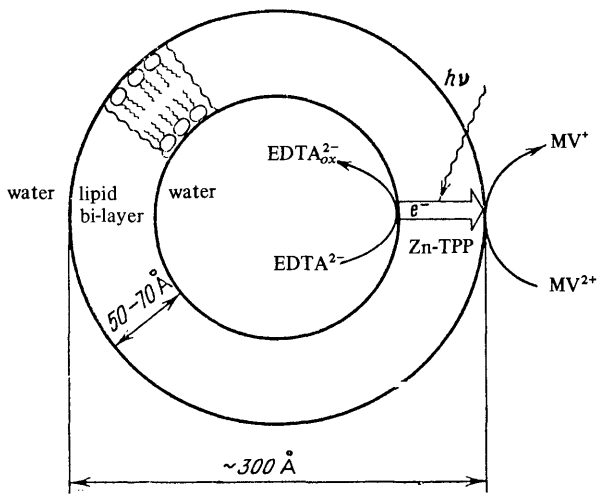


Figure 10. Scheme of the photo-transfer of an electron through the membranes of lipid vesicles containing Zn-TPP as photocatalyst.

The vesicles, whose structure is shown schematically in Fig.10, consist of a shell formed by a two-layer lipid membrane. The vesicles described below were prepared by using either the natural lipid lecithin or the synthetic lipid dipalmitoylphosphatidylcholine (DPPC). The inner cavity of the vesicles was filled with an aqueous solution of electron donors (the sodium salt of ethylenediaminetetra-acetic acid, Na-EDTA, or nicotinamide dinucleotide, NADN), whereas the outer volume contained an electron acceptor (methylviologen, MV^{2+}). It has been convincingly shown[81,96–99] that irradiation of solutions of vesicles containing photo-catalysts in the membrane can produce electron transfer across the membrane, leading to the formation of D^+ and A^- species which are prevented from recombining by being on opposite sides of the membrane. The photocatalysts used in these experiments had long hydrophobic groups: chlorophyll[97,100], or surface-active derivatives of zinc porphyrin[98] or of the *tris*-bipyridyl ruthenium complex[81,96,99]. The photo-catalyst used in our work was much simpler, and did not contain long hydrophobic groups: zinc tetraphenylporphin (Zn-TPP).[101–104]

Irradiation of a solution of vesicles with light of wavelength corresponding to the Soret band of Zn-TPP ($\lambda \cong 425$ nm) or to its long-wave absorption bands ($\lambda > 500$ nm) causes photo-transfer of electrons from the donor particles within the vesicle to acceptor particles outside it (see Fig.11), the metallo porphyrin contributing repeatedly to the cycle in which MV^{2+} is reduced by the electron donors and thus behaving as a true photocatalyst[101]. The quantum yield of the reduction of MV^{2+} in the natural lecithin system irradiation with focussed filtered light from a DKSSh-1000 lamp in the region of the Soret band or of the long-wave absorption bands was 0.01 to 0.1%, the highest observed quantum yield (for light in the long-wavelength absorption band region) being 0.15 ± 0.04%.[104]

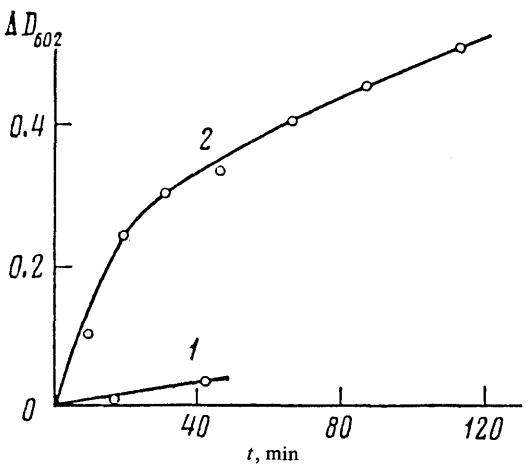


Figure 11. Change in optical density at $\lambda = 602$ nm due to the accumulation of MV^+ during irradiation by light with $\lambda > 500$ nm (from a DRSh-1000 lamp) of a solution of egg lecithin vesicles containing Zn-TPP: curve *1* was obtained in the absence of electron donors, curve *2* in the presence of 0.2 M Na_2-EDTA inside the vesicles[101]. The concentration of lecithin, Zn-TPP, and MV^{2+} are (respectively) 2.4×10^{-3} g cm^{-3}, 6×10^{-5} M, and 2×10^{-2} M; temperature 298 K. When a synthetic lipid was used the accumulation of MV^+ in the absence of Na_2-EDTA was negligible.

The observation of electron photo-transfer across a membrane by light of wavelength corresponding to the long-wave absorption bands, i.e. under the influence of quanta able to excit only the first singlet level of Zn-TPP, is evidence of the important part played by the lower excited states of Zn-TPP in the electron photo-transfer process.

In the flash photolysis of a solution of vesicles containing only Zn-TPP but no electron donors or acceptors the transient optical spectrum shows an absorption assigned to the triplet electronically excited state of porphyrin ($Zn\text{-}TPP^T$) and to the porphyrin cation radical ($Zn\text{-}TPP^+$). The very fast deactivation of the triplet states is probably caused by the annihilation reaction

$$2Zn\text{-}TPP^T \longrightarrow 2Zn\text{-}TPP + \Delta E \qquad (8)$$

The rate of this process is much higher in the vesicle solution than in a homogeneous solution containing the same total amount of porphyrin because of the high local concentration of porphyrin in the lipid bi-layer (up to 2.5×10^{-2} M, i.e. well in excess of the average concentration). The cation radical Zn-TPP^{+} may also be produced by the annihilation of triplet states:

$$2\text{Zn-TPP}^{T} \rightarrow \text{Zn-TPP}^{+} + \text{Zn-TPP}^{-} \quad (9)$$

Unfortunately we were unable to detect the anion radical Zn-TPP^{-} directly because of the strong absorption of the triplet states in the region of the characteristic absorption lines of Zn-TPP^{-}.

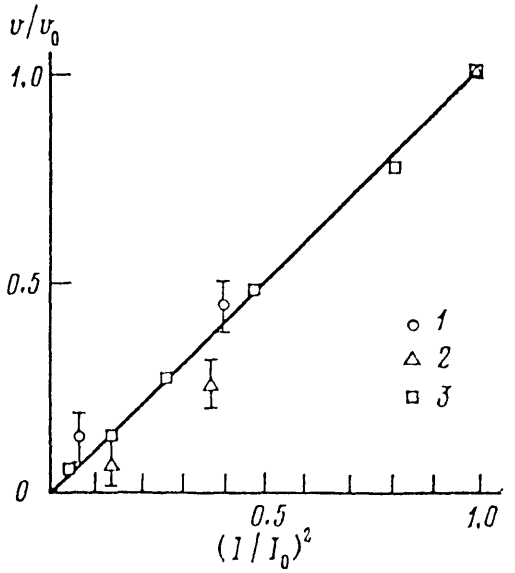


Figure 12. Initial rate (v) of accumulation of MV^{+} in a solution of lipid vesicles against the intensity (I) of exciting light for irradiation in the region of the Soret band (*1*, *3*) and of the long-wave absorption bands (*2*) of zinc porphin: *1*) and *2*) refer to vesicles of natural lecithin, under the conditions stated in Fig.11, *3*) refers to vesicles of synthetic DPPC, with concentrations of DPPC and MV^{2+} of 5×10^{-3} g cm^{-3} and 0.1 M respectively, [Zn-TPP] : : [DPPC] = 1 : 50, other conditions as in Fig.11;[101,102] v_0 is the initial rate of accumulation of MV^{+} for a light intensity I_0.

When MV^{2+} is present outside the vesicles a strong and long-lived absorption due to the cation radicals MV^{+} and Zn-TPP^{+} is observed immediately after the flash. The disappearance (by recombination) of these products of the flash photolysis takes place in parallel, and is described by a second-order equation with rate constant $k = (1.9 \pm 0.2) \times 10^{8}$ litre mole^{-1} s^{-1}. In this way the concentrations of MV^{+} and Zn-TPP^{+} immediately after a flash $\leq 10^{-5}$ s long are about one-quarter of the concentration of Zn-TPP in the sample, i.e. they are much higher than the concentration of Zn-TPP^{+} observed immediately after the same flash but in the absence of MV^{2+}. The large amount of MV^{+} formed and its disappearance by a second-order reaction (i.e. by interaction with extraneous cation radicals rather than with the cation radicals of the matrix Zn-TPP^{+}) suggest that both the formation of MV^{+} and its migration from the reaction cage after the electron photo-transfer act have a high probability.

The presence of EDTA^{2-} as the sodium salt inside the vesicle has no effect on the flash photolysis of vesicles containing Zn-TPP, both in the presence and in the absence of MV^{2+} in the outer solution.

The one-quantum[81,96,97] and the two-quantum[98] mechanisms for the activation of photo-transfer through the membranes of lipid vesicles have been discussed in published papers. For both the natural and the synthetic lipid (at 287–333 K) we have observed[103] a square-law dependence of the initial rate of accumulation of MV^{+} on the intensity of the exciting light (Fig.12), which suggests a two-quantum mechanism for the photo-transfer involving Zn-TPP over the whole range of temperature. This dependence is observed with light of wavelength in the region of both the Soret band and the long-wave absorption bands of Zn-TPP, and therefore it is not related to the nature of the primary singlet-excited state. This suggests that the photo-transfer process involves the triplet-excited Zn-TPP molecules. It is interesting to note that when EDTA^{2-} is present on the same side (the outside) as MV^{2+}, i.e. when the membrane is used merely as a carrier of the water-insoluble photocatalyst Zn-TPP, the initial rate of accumulation of MV^{+} is linearly dependent on the light intensity, denoting a one-quantum mechanism for the photo-transfer of an electron from EDTA^{2-} to MV^{2+}.

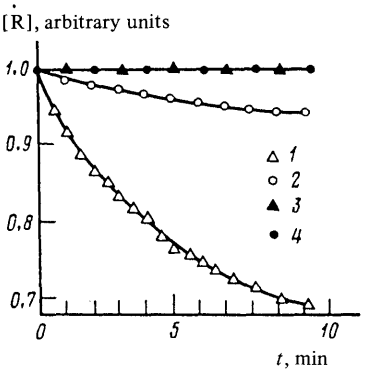
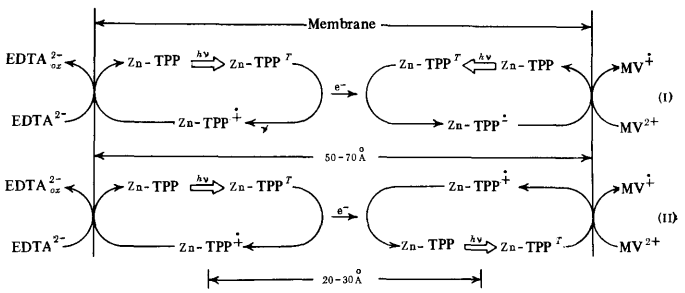


Figure 13. Kinetics of the photo-reduction of Doksil spin probes (Ṙ) trapped in vesicles of synthetic DPPC with (*1*, *2*) and without (*3*, *4*) zinc porphin in the bi-layer. Concentrations of the lipid and of Na_2-EDTA 10 mg cm^{-2} and 0.2 M respectively, [Zn-TPP] : [DPPC] = 1 : 50, [spin probe] : [lipid] = 1 : 200, 298 K. Spin probes: *1*) and *3*) 5-DOKSIL, *2*) and *4*) 16-DOKSIL.[102]

In order to determine the mechanism of electron photo-transfer through the membrane we need to establish the location of the electronically excited porphyrin molecules within the lipid bi-layer, since in principle they could be evenly distributed throughout the thickness, localised near the centre, or localised near the surface. We tried to answer this question by studying the irreversible photo-reduction of amphiphilic Doksil spin probes (a stearic acid derivative) localised in the vesicle membrane, interacting with electronically excited Zn-TPP molecules[102]. We found that under comparable conditions the rate of photo-reduction of the spin probes having an ṄO fragment near the surface of the

bi-layer (i.e. those with a paramagnetic substituent on the fifth carbon atom from the carboxyl group, "5-Doksil") is much greater than the rate of reduction of the probes with the $\dot{N}$–O fragment deep within the bi-layer (with their paramagnetic substituent on the 16th carbon atom, "16-Doksil") (see Fig. 13). Since the rate of photo-reduction of the $\dot{N}$–O fragments must increase with decreasing distance to the electronically excited Zn-TPP molecule we may conclude that the latter is preferentially localised near the surface of the bi-layer.

From these results we may suggest two alternative schemes for the phototransfer of an electron through the membrane which are consistent with both the steady-state and the flash photolysis data:



(where the symbol $EDTA^{2-}_{ox}$ refers, as before, to the products of the irreversible oxidation of $EDTA^{2-}$). According to scheme (I) the process responsible for the electron transfer through the membrane are the annhiliation of two Zn-TPP^T molecules with formation of Zn-TPP$^+$ and Zn-TPP$^-$ and the subsequent reactions of these ion radicals with $EDTA^{2-}$ and MV^{2+}. According to scheme (II) the electron transfer through the membrane is due to the reaction between Zn-TPP^T and MV^{2+}, followed by the transfer of an electron to the Zn-TPP$^+$ formed near the outer surface of the vesicle from another Zn-TPP^T particle near the inner surface, and lastly by the interaction of the resulting Zn-TPP$^+$ and $EDTA^{2-}$ particles. In both cases a square-law dependence of the initial rate of accumulation of MV^+ on the light intensity can be expected.

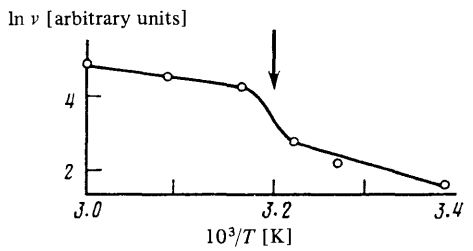


Figure 14. Temperature dependence of the initial rate (ν) of accumulation of MV^+ in a solution of synthetic DPPC vesicles. Concentrations of lipid, Zn-TPP, and MV^{2+} 1.5×10^{-3} g cm^{-3}, 3.7×10^{-5} M, and 2×10^{-2} M respectively; concentration of Na_2-EDTA in the cavity of the vesicles 0.2 M. Irradiation with light in the region of the long-wave absorption bands of Zn-TPP. The arrow denotes the temperature of the phase transition of the lipid (~315 K).[103]

The published values[105] of the redox potentials of the species involved in these schemes suggest that both variants are thermodynamically possible.

As was shown above, the presence of MV^{2+} outside the vesicles causes a large increase in the initial concentration of Zn-TPP$^+$ during flash photolysis. This means that the transfer of an electron from Zn-TPP^T to MV^{2+} (on the outer surface of the vesicle) is a more effective channel for the disappearance of Zn-TPP^T than reaction (9) under the present conditions. Therefore we consider scheme (II) to be the more realistic. The diffusion of a charged photolysis intermediate (Zn-TPP$^+$) in the non-polar lipid membrane is probably slow. Under these conditions electron transfer through the membrane can occur, for example, by a tunnelling exchange between Zn-TPP and Zn-TPP$^+$. It is interesting to note that when the temperature is lowered through the melting point of the lipid the rate of photo-transfer of electrons through the membrane drops sharply but does not fall to zero (Fig. 14).[103] A similar effect (electron transfer at a significant rate below the freezing point of the system) had been observed earlier for the recombination of light-separated charges in the photo-system I of plants (see, for example, Ref. 106, and also Ref. 107 and its list of references).

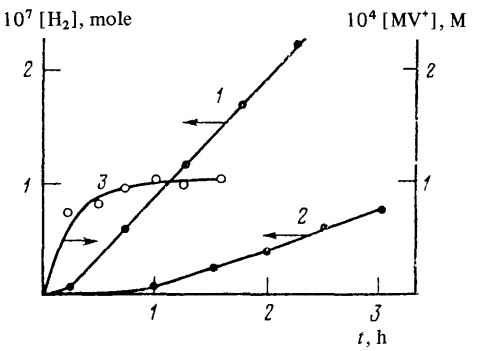


Figure 15. Kinetics of the accumulation of hydrogen over 1 cm^3 of a solution of egg licithin lipid vesicles containing Zn-TPP in the lipid bi-layer, a 0.2 M solution of Na_2-EDTA in the vesicle cavities, and in the outer volume MV^{2+} and a hydrogen evolution catalyst (*1*, *Tiocapsa roseopersicina* hydrogenase; *2*, activated Rh–AN-221 heterogeneous catalyst). Irradiation with light of $\lambda > 510$ nm from a DKSSH-1000 lamp; concentration of lipid, Zn-TPP, and MV^{2+} 6.7 mg cm^{-3}, 1.7×10^{-4} M, and 4.3×10^{-3} M respectively; temperature 303 K. Curve *3* shows the development of a steady-state concentration of MV^+ in the presence of hydrogenase (measured in parallel with the kinetic curve *1*). A pH of 7.2 was maintained both within and outside the vesicles by an ammonium buffer[104].

The continuing square-law dependence of the rate of photo-transfer of electrons through the membrane on the light intensity below the phase transition temperature of the lipid suggests that the mechanisms are similar at temperatures above and below the phase transition. The stepwise change in rate at the transition point is probably due to the unfreezing of the lateral diffusion modes of the reactants caused by the melting of the lipid. We note that a similar (stepwise) change in rate with temperature is found by flash photolysis in this system even for long-range interactions such as the triplet–triplet deactivation of excited porphyrin molecules [reaction (8)].[103]

The similarity between the mechanism of charge photo-separation by scheme (II) and the mechanism of charge photo-separation now generally accepted ("Z-scheme") for photosynthesis in plants is unmistakable. The vesicles containing metallo-porphyrins can therefore be treated as analogues of biological charge photo-separation systems, and a substantial increase in quantum yield may therefore be expected (by analogy with those systems) by suitable choice of photocatalyst, electron donor and acceptor, and lipid.

The photo-reduction of MV^{2+} by the electron donors $EDTA^{2-}$ or NADN is endothermic, and therefore (with NADN, for example) each act of photo-transfer is accompanied by the storage of 0.12 eV of energy. For irradiation with light of wavelength in the region of the long-wave absorption bands of Zn-TPP this corresponding to a storage of ~3% of the combined energy of the two light quanta needed for the photo-transfer of an electron.

Thus by inserting a fairly simple photocatalyst (zinc tetraphenylporphin) into the lipid membrane we can induce electron photo-transfer through the membrane by visible light (admittedly, so far, in low quantum yield). The reduced form of the electron acceptor used in our experiments, MV^{+}, can evolve molecular hydrogen from water even at neutral pH values in the presence of suitable catalysts. We were able to observe this process (at pH ~ 7) by adding to the solution outside the vesicles the hydrogenase enzyme *Thiocapsa roseopersicina* at ~10^{-6} M concentration, or the heterogeneous catalyst Rh–AN-221 (described above) in an activated form[104]. The effective quantum yield of the photo-catalytic hydrogen evolution measured in the stationary region (Fig.15) was $(1.0 \pm 0.3) \times 10^{-2}$% in the first case and $(0.3 \pm 0.1) \times 10^{-2}$% in the second. By comparing these values with the measured quantum yield of MV^{+} $(4.0 \pm 1.0) \times 10^{-2}$% on the initial portion of the kinetic curve for its formation, and under similar conditions, we conclude that the efficiency of the "dark" catalytic processes developed for these systems is already relatively high. The reason for the lower quantum yield of hydrogen (as compared with the yield of MV^{+}) is still not clear, though we should see that because of the stoichiometry of reaction (3) the quantum yield of hydrogen cannot be greater than one-half the quantum yield of MV^{+}: one possible cause is the screening effect on the photo-catalyst by the added hydrogen evolution catalysts.

Although the oxidation potential of the oxidised forms of these donors is insufficient to evolve oxygen from water, we note that the oxidation potential E_0 of one of the intermediates ($Zn\text{-}TPP^{+}$, $E_0 = +1.0$ V with respect to the NHE [105]) is high enough if a pH $\geq$ 5 is maintained inside the vesicle. This justifies the hope that the full water decomposition cycle may be realised in the near future in a system based on Zn-TPP and related metallo-porphyrins by optimising the choice of electron donors.

Knowing the mechanism of electron photo-transfer through a bi-layer membrane containing Zn-TPP should assist the solution of important problems such as maximising the quantum yield of the electron photo-transfer and improving the spectral sensitivity of the process, since (at $\lambda > 450$ nm, for example) the useful spectral range is limited by the relatively narrow absorption bands of Zn-TPP (total width 50–100 nm).

Thus, if scheme (II) is correct the rate of electron photo-transfer through the membrane should increase with the rate of regeneration of Zn-TPP molecules from the cation radical $Zn\text{-}TPP^{+}$ formed by the photo-transfer, and with the rate of excitation of Zn-TPP molecules on the inner surface of the membrane by energy transfer through some "antenna", analogous to the chlorophyll molecules in the chloroplasts of plants. We achieved this by using the complex $Ry(bipy)_3^{2+}$ at a concentration of ~0.07 M in the inner cavity of the lecithin vesicles[108] as a sensitising additive, able in principle to bring about both the transfer of an electron from the inner cavity to the $Zn\text{-}TPP^{+}$ and the transfer of energy to Zn-TPP. At this concentration of $Ru(bipy)_3^{2+}$ the absorption spectrum of the vesicle solution contains (in addition to strong Zn-TPP absorption bands) a fairly strong absorption band at $\lambda \cong 460$ nm due to the added sensitiser.

Irradiation of this combined system (containing both Zn-TPP and $Ru(bipy)_3^{2+}$) with light of $\lambda > 415$ nm, which excites both these photosensitive complexes, results in much faster electron photo-transfer through the membrane. Under these conditions we observed the highest ever quantum yield (~0.6%) for the photo-transfer through a membrane to MV^{2+} of an electron in vesicles containing a photocatalyst inside a lipid bi-layer. The quantum yield was calculated as the ratio of the initial rate of electron photo-transfer to the total number of quanta absorbed by the system (i.e. allowing for the absorption of both $Ru(bipy)_3^{2+}$ and Zn-TPP).

The details of the mechanism by which $Ru(bipy)_3^{2+}$ sensitises this system are being studied at the moment. We shall only note that if this sensitising effect is associated with the formation of the strong oxidiser $Ru(bipy)_3^{3+}$ (for which $E_0 = +1.3$ V relative to the NHE) in the inner cavity of the vesicle, for example by a reaction such as

$$Zn\text{-}TPP^{+} + {}^{*}Ru(bipy)_3^{2+} \rightarrow Zn\text{-}TPP + Ru(bipy)_3^{3+})$$

it should be possible (by an appropriate choice of homogeneous catalyst, e.g. a cobalt or iron complex, see Section III) to evolve oxygen from water in the cavity of the vesicle and thus complete the cycle of the photocatalytic decomposition of water.

Indeed, we have found[108] that the processes in this system are affected by the presence of cobalt chloride (an active oxygen evolution homogeneous catalyst) in the inner cavity of vesicles sensitised by the ruthenium complex. Thus, if the Na_2-EDTA solution in the cavity is replaced by a $(1–5) \times 10^{-4}$ M solution of $CoCl_2$ in a borate buffer (pH 9) to allow oxygen evolution a small quantity of MV^{+} is formed during irradiation of the system: if other conditions are kept constant the initial rate of accumulation is always greater in the presence of $CoCl_2$ than in its absence (when, as stated above, the accumulation of MV^{+} is due to the irreversible oxidation of impurities in egg lecithin).

We may suggest that in the presence of $CoCl_2$ the strong oxidiser $Ru(bipy)_3^{3+}$ produced by the irradiation contributes to the catalytic oxidation of water, which under these conditions may be faster than the oxidation of the impurities. However, a final judgement on the possibility of oxidation of water in the inner cavities of vesicles sensitised by $Ru(bipy)_3^{2+}$ must await direct experimental evidence on the presence (or absence) of evolved oxygen.

We note that after the addition of $Ru(bipy)_3^{2+}$ to the vesicle cavity the scheme proposed for this system becomes even more similar to the "Z-scheme" of natural photosynthesis: on the outer surface of the membrane we find the analogue of "photo-system I", and on the inner surface the analogue of "photo-system II".

Some of our latest results[109] show that $Ru(bipy)_3^{2+}$ within the inner cavity of vesicles can act as a photocatalyst and induce electron transfer even if the membrane is "photo-passive" (i.e. if the lipid bi-layer does not contain a photocatalyst). This photo-transfer takes place in the prescence of photo-inactive compounds (electron carriers) able to penetrate into the lipid bi-layer or to pass through it carrying an electron from the electronically excited state of $Ru(bipy)_3^{2+}$.

Thus when $Ru(bipy)_3^{2+}$ ions in the cavity of lecithin vesicles are excited by light together with the irreversible electron donor $EDTA^{2-}$, and if the lipid membrane contains the water-insoluble electron carriers cetylviologen dibromide

(N,N'-dicetyl-4,4'-dipyridine, CV^{2+}) or decylviologen (N,N'-didecyl-4,4'-dipyridine) we observe photocatalytic transfer of an electron from $EDTA^{2-}$ in the inner cavity to the reversible electron acceptor $Fe(CN)_6^{3-}$ in the outer volume of the vesicle, which cannot pass through the lipid membrane. The quantum yield of the electron photo-transfer to $Fe(CN)_6^{3-}$ is strongly dependent on the concentration of the electron carrier in the membrane, reaching (2.3 ± 0.5)% in the case of CV^{2+} for a molar ratio of CV^{2+} : lipid = 1 : 100, and (15 ± 5)% for a molar ratio of CV^{2+} : lipid = 1 : 20 (temperature 293 K, excitation of the $Ru(bipy)_3^{2+}$ by monochromatic light of wavelength 488 nm at a radiation density of 1.0 W cm^{-2}. local concentrations of $Ru(bipy)_3^{2+}$, $EDTA^{2-}$, and $Fe(CN)_6^{3-}$ 1.6×10^{-3}, 0.2, and 10^{-3} M respectively).

Photocatalytic electron transfer through these membranes was observed also after replacing the $Fe(CN)_6^{3-}$ outside the vesicle by two-electron acceptors such as the water-soluble dyes of the phenothiazine series (Methylene Blue, thionine); the quantum yield of the electron transfer through the lipid bi-layer under these conditions was again of the order of several per cent.

We should stress that the quantum yields for electron transfer quoted above are much higher than the usual values for the "photo-active" membrances (containing a photo-catalyst within the membrane) discussed in this review. Therefore the long-term prospects of photocatalytic systems based on photo-passive membranes are also good.

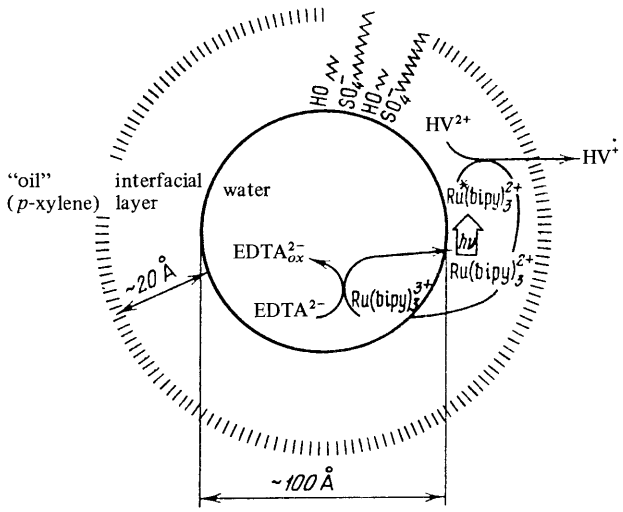


Figure 16. Scheme of the photo-transfer of an electron between phases in an anionic ME-I micro-emulsion of the "water in oil" type containing heptylviologen (N,N'-diheptyl-4,4'-dipyridine) HV^{2+}, $Ru(bipy)_3^{2+}$, and $EDTA^{2-}$.

2. Charge Separation in Micro-emulsions

The recombination of the products of reaction (1) can be suppressed also by using micro-emulsions of the "water in oil" type. We have studied the following micro-emulsion compositions (in wt.%): p-xylene (60.8%), n-pentanol (22.0%), sodium dodecyl sulphate (3.6%), and water (13.6%) (micro-emulsion ME-I [110,111]), and also toluene (71.3%), n-pentanol (7.4%), decylammonium propionate (9.1%), and water (12.2%) (micro-emulsion ME-II [111]). Both are transparent, slightly opalescent solutions containing water drops ~100 Å in diameter in p-xylene [112] or toluene. These droplets are surrounded by a layer on n-pentanol molecules and partially dissociated molecules of sodium dodecyl sulphate (SDS) in the emulsion ME-I, or of decylammonium propionate (DAP) in ME-II, which create an interface ~20 Å thick. The structure of ME-I is shown in Fig. 16.

The photocatalysts added to the micro-emulsion were the complex $Ru(bipy)_3^{2+}$ or its surface-active analogue $Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$, which differs from $Ru(bipy)_3^{2+}$ in having one bipyridyl ligand replaced by a bipyridyl derivative (4-methyl-4'-heptadecyl-2,2'-bipyridyl) with a long hydrophobic cetyl chain in the fourth position[113]. By comparing data on the rate of fluorescence quenching of the ruthenium(II) complexes in homogeneous aqueous solutions and in micro-emulsions by substances readily soluble in water but poorly soluble in p-xylene or toluene (see Table 4) we conclude that the ruthenium photocatalysts are found mainly at the interface. Thus the large decrease in the quenching rate constant produced by changing from homogeneous solutions to micro-emulsions shows that the photocatalysts are not localised in the aqueous phase. On the other hand they cannot be localised in the organic phase, because if they were they could not interact with the quenchers (which are in the water phase) with the observed rate constants of $k_q \geq 10^7$ litre $mole^{-1}$ s^{-1}.

Table 4. Rate constants k_q for the luminescence quenching of ruthenium(II) complexes in homogeneous solutions and in micro-emulsions at 297 K .

Complex	A	10^3[A], M	10^{-8} k_q, litre $mole^{-1}$ s^{-1}
	medium: water		
$Ru(bipy)_3^{2+}$	MV^{2+}	5	4.7
$Ru(bipy)_3^{2+}$	HV^{2+}	5	8.0
	medium: ethanol + toluene (1 : 1)		
$Ru(bipy)_3^{2+}$	CV^{2+}	1	6.1
	medium: ME-I		
$Ru(bipy)_3^{2+}$	MV^{2+}	4—25	0.8
$Ru(bipy)_3^{2+}$	HV^{2+}	4—25	0.5
$Ru(bipy)_3^{2+}$	CV^{2+}	3	2.5
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	MV^{2+}	4—25	0.5
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	HV^{2+}	4—25	0.9
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	CV^{2+}	3	4.6
	medium: ME-II		
$Ru(bipy)_3^{2+}$	CV^{2+}	1	8.0
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	CV^{2+}	1	8.8

Notes. A is the quencher. For the micro-emulsions the local concentrations of the water-soluble MV^{2+} and HV^{2+} are given on the assumption that these species are present only in the water phase. In the case of the water-insoluble CV^{2+} the concentration is calculated in terms of the whole volume. The effective bimolecular quenching rate constants were obtained by dividing the quenching rate by the concentrations as defined above.

Irradiation with visible light ($\lambda > 450$ nm) of the micro-emulsion ME-I containing, in addition to the photocatalyst [$Ru(bipy)_3^{2+}$, 6×10^{-5} M], an electron acceptor (heptylviologen, HV^{2+}, 3×10^{-4} M) and an electron donor (Na_2-EDTA, 6×10^{-3} M) localised mainly in the water phase, causes accumulation of the cation radicals HV^{+} with a quantum yield of

~1%.[110] In the absence of Na_2-EDTA or of the ruthenium complex no HV^{+} is formed. Photolysis of a homogeneous aqueous solution containing $Ru(bipy)_3^{2+}$, HV^{2+}, and Na_2-EDTA produces a violet precipitate of water-insoluble HV^{+} which can be extracted easily and quantitatively by a mixture of *p*-xylene and n-pentanol in the same ratio as in the micro-emulsion. This shows that the HV^{+} cation radical formed by photolysis of the ME-I micro-emulsion must also reside mainly in the organic phase. The electron donors ($EDTA^{2-}$ anions) cannot be accommodated in the interface (saturated with SDS anions) or in the non-polar organic phase, and therefore they can only be in the aqueous phase of the micro-emulsion. Since we are able to achieve almost complete reduction of HV^{2+} to HV^{+} it appears that the $Ru(bipy)_3^{2+}$ present at the interface in an amount five times smaller than the heptylviologen acts as a true photocatalyst for the transfer of an electron from the donor $EDTA^{2-}$ (localised in the water phase) to the acceptor HV^{2+} (whose reduced form is extracted into the organic phase).

Flash photolysis of a homogeneous aqueous solution containing only $Ru(bipy)_3^{2+}$ and HV^{2+} produces the cation radical HV^{+}, whose concentration then decreases as a result of recombination with the oxidiser $Ru(bipy)_3^{3+}$ formed together with the HV^{+}. The disappearance of HV^{+} obeys the law of second-order kinetics with a rate constant $k = (1.5 \pm 0.1) \times 10^9$ litre^{-1} s^{-1} up to an extent of reaction of 99%. In contrast, the decrease in optical density of HV^{+} after flash photolysis of an ME-I micro-emulsion containing only $Ru(bipy)_3^{2+}$ and HV^{2+} is kinetically more complex (see curve *1* of Fig.17). At short times we observe a bimolecular disappearance of HV^{+} with a rate constant $k = (1.2 \pm 0.1) \times 10^9$ litre mole^{-1} s^{-1}, but after ~1 ms the disappearance of HV^{+} slows down and the bimolecular law is not obeyed.

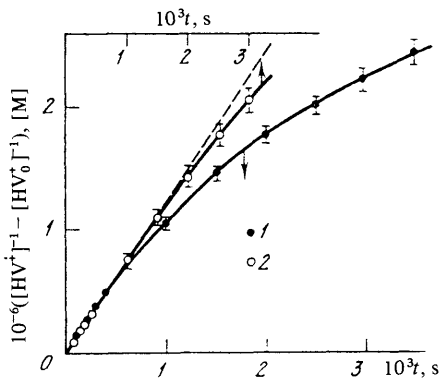


Figure 17. Kinetic curves for the recombination of HV^{+} with $Ru(bipy)_3^{3+}$ (*1*) and of HV^{+} with $Ru(C_{17}\text{-bipy})(bipy)_2^{3+}$ (*2*) after flash photolysis of an ME-I micro-emulsion containing 3.1×10^{-3} M HV^{2+} and 2.5×10^{-4} M ruthenium complexes; temperature 298 K. The broken line denotes second-order kinetics with the rate constants calculated from the initial portions of the experimental kinetic curves[110].

This type of recombination kinetics can be explained as follows (a more detailed analysis can be found in Ref.110). During the photolytic flash one of the primary products of electron photo-transfer at the interface (the species HV^{+}) can distribute itself between the interface and the organic phase in accordance with its solubility, whereas the second product [$Ru(bipy)_3^{3+}$] diffuses slowly into the aqueous phase where it can oxidise $EDTA^{2-}$ if this species is present. The initial portion of the kinetic curve, described by the bimolecular law, corresponds to recombination of the HV^{+} with the $Ru(bipy)_3^{3+}$ which has not yet migrated into the water phase. The slowing down of the recombination observed at long times shows that some of the oxidiser $Ru(bipy)_3^{3+}$ has migrated away from the sphere of action and is no longer available to recombine with the HV^{+} in the interfacial layer.

This explanation of the shape of curve *1* in Fig.17 suggests that the replacement of $Ru(bipy)_3^{2+}$ by the more lyophilic complex $Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$ should result in less marked deviations of the recombination kinetics from the bimolecular law, since the transfer of the oxidised form of the photocatalyst from the interface to the aqueous phase would then be hindered. As curve *2* of Fig.17 shows, this prediction is borne out in practice.

Table 5. Recombination rate constants k and relative probabilities P/P_0 of the oxidiser and the reducer formed by electron photo-transfer from a donor to an acceptor emerging from the original pair in homogeneous aqueous solutions and in micro-emulsions at 298 K.[111]

Donor	Acceptor	$10^8\,k(\pm1)$, $M^{-1}\,s^{-1}$	P/P_0
	medium: water		
$Ru(bipy)_3^{2+}$	MV^{2+}	17	1.00
$Ru(bipy)_3^{2+}$	HV^{2+}	15	0.95
	medium: ME-I		
$Ru(bipy)_3^{2+}$	MV^{2+}	25	0.24
$Ru(bipy)_3^{2+}$	HV^{2+}	12	0.67
$Ru(bipy)_3^{2+}$	CV^{2+}	12	0.15
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	HV^{2+}	7.8	0.35
ditto	CV^{2+}	8.0	0.15
	medium: ME-II		
$Ru(bipy)_3^{2+}$	CV^{2+}	2.7	2.8
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	CV^{2+}	6.7	0.7

Notes. In the case of water solutions the k values are given for a low ionic strength ($\mu < 0.05$ M); P_0 is the probability of the electron photo-transfer products emerging from the original pair in the $Ru(bipy)_3^{2+}$–MV^{2+} system in aqueous solution; the precision of the measurements of P/P_0 is ±10%.

Thus, owing to the fast extraction of HV^{+} into the organic phase coupled with a much slower migration of $Ru(bipy)_3^{3+}$ into the water phase, some of the primary products of the electron photo-transfer process are in different phases, and as a result their recombination is suppressed. These results justify the hope that effective segregation of the products of primary electron photo-transfer into different phases may be achieved in the near future by varying the electric charge of the interfacial layer of the micro-emulsion and the hydrophilic and oleophilic properties of the primary electron donor and acceptor (by introducing appropriate substituents).

Thus, by varying these properties we should be able to control the two most important parameters of the system, responsible in the final analysis for effectiveness of the extraction of the primary charge separation products: the effective rate constant k for the recombination of the primary oxidiser and reducer in the interfacial layer of the micro-emulsion and the probability P of the oxidiser and the

reducer breaking away from their initially paired configuration. We note that a marked deviation of the parameter P from unity is the most usual explanation of small quantum yields in bimolecular oxidation–reduction reactions involving excited states. Our values[111] of k and P for the micro-emulsions ME-I (with a negatively charged interfacial layer) and ME-II (positively charged layer) are listed in Table 5 for different pairs of electron donor and electron acceptor having different lyophilicities. The rate constant k was measured from the initial slope of the kinetic curve for the recombination of the primary oxidiser and reducer, recorded by the flash photolysis method. The probability P was determined by comparing the initial concentrations of the reduced forms of the viologens, observed immediately after a photolytic light flash of duration less than 10^{-5} s, with the concentration of MV^{+} observed under similar conditions in a homogeneous aqueous solution containing $Ru(bipy)_3^{2+}$: the absolute value of the probability P for the $Ru(bipy)_3^{2+}$–MV^{2+} system in water was found[114] to be 25%.

It is clear from Table 5 that, as expected, the best results (i.e. a more than six-fold decrease in k and an almost three-fold increase in P to $P = 2.8 \times 25\% = 70\%$ as compared with a homogeneous aqueous solution) are obtained in micro-emulsions with a positively charged interface if the electron donor has a low lyophilicity [$Ru(bipy)_3^{2+}$] and the electron acceptor has the highest possible lyophilicity (cetylviologen, CV^{2+}). A positive charge on the interface of the micro-emulsion prevents the charge separation products of the same (i.e. positive) sign from recombining at the phase boundary.

We note that in a really effective photo-catalytic system the recombination of the D^{+} and A^{-} particles created by reaction (1) should be slow enough to allow reactions (2) and (3) to proceed, with evolution of hydrogen and oxygen. We should stress that the reduced forms of HV^{+} and CV^{+} (like the reduced form MV^{+}) can evolve hydrogen from water in the presence of the catalysts discussed in Section II; the prospects of the evolution of oxygen from water by $Ru(bipy)_3^{3+}$ and its analogues are discussed in Section III.

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This general assessment of the present state of photocatalytic converters of solar energy into chemical energy by exploiting the water decomposition reaction shows that the development of effective charge separation systems continues to be the major problem facing the creation of practical molecular photocatalytic systems for decomposing water into hydrogen and oxygen. We may hope that as soon as these systems are discovered the efficient decomposition of water by sunlight under laboratory conditions will be a practical possibility.

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The Thermodynamics of the Formation of Outer-sphere Complexes in Solution

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Data on the thermodynamics of the formation of outer-sphere complexes of coordination compounds of cobalt(III), rhodium(III), iridium(III), platinum(IV), chromium(III), iron(II), ruthenium(II), (III), and osmium(II) have been reviewed. Various regular features of outer-sphere complex formation by inert hydrophilic and hydrophobic cationic complexes with d^6, d^5, and d^3 electron configurations of the central metal ion in aqueous and aqueous-organic solutions have been established. The bibliography contains 144 references.

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I. INTRODUCTION

The formation of outer-sphere complexes[1] is a widespread phenomenon, since most inner-sphere complexes form outer-sphere associates, depending on the composition of the surrounding medium. Detailed studies of outer-sphere complexes (OSC) carried out in recent years have revealed the characteristic features of their formation and new possibilities for their practical application, and this has led to an increased interest in the comprehensive study of OSC.[2]

In the last 15 years, several reviews of the stability and structural characteristics of OSC in solution have been published[2-8]. Reference has been made[1] to a monograph on this topic[9], but this has not yet appeared.

Outer-sphere complexes can be divided into two groups. The first group consists of compounds formed by inert, and the second group of compounds formed by labile (in Taube's terminology) [10] inner-sphere complexes. The OSC of both groups are characterised by high rates of formation and dissociation of the outer coordination sphere[11], that is this sphere is always labile. A large proportion of studies have been carried out for OSC formed by inert coordination compounds. In a number of cases, as a consequence of differences in the rate of formation or in the stability of the inner and outer spheres, it is also possible to carry out qualitative and semi-quantitative studies of the thermodynamics of the formation of OSC by labile inner-sphere complexes[11-18].

Most present-day and earlier studies of OSC have been carried out at a single temperature[19,20]. Only in a few studies have the measurements been made at several temperatures, and the enthalpy and entropy changes for the formation of the OSC calculated from the temperature dependence of the equilibrium constants. The enthalpy changes on OSC formation are small ($<\pm 20-40$ kJ mole^{-1}), and the temperature-coefficient method gives appreciable errors in the determination of small thermal effects[21,22]. Accurate values of the enthalpy and entropy changes can be obtained only by direct thermochemical measurements using highly sensitive calorimeters. Up to the present, all such measurements (except of the heats of two reactions[23]) have been carried out only in the laboratory of the authors of the present review. The aim of the present work is to summarise and discuss critically the data obtained on the thermodynamics of the formation of OSC and to examine other studies of similar content.

Data on the thermodynamics of the formation of OSC by inert cationic complexes of cobalt(III), rhodium(III), iridium(III), platinum(IV), chromium(III), iron(II), ruthenium(II), (III), and osmium(II) are reviewed. Almost all the data relate to aqueous solutions. Some information on outer-sphere interactions in aqueous-organic solvents is also given.

An unsymmetrical standard state[24,25] (that is different for the solvent and the solutes) is used in the study of solutions of electrolytes in general and of OSC in particular. A hypothetical molal (molar) solution with the properties of an infinitely dilute solution is taken as standard for OSC (and for their components). The state of the pure liquid at a definite temperature and pressure is taken as the standard state for the solvent.

The recalculation of the values of the stability constants of the OSC and the enthalpy changes for their formation (from solutions with definite ionic strengths of constant magnitude to the standard state indicated above) is carried out[26] using Vasil'ev's equations[27,28].

The problem of selecting inert salts to keep the ionic strengths constant is solved in various ways. The experience of a large number of studies has shown[26,29] that the perchlorate anion is the most "inert" with respect to hydrophilic cationic complexes, and the fluoride anion the most inert with respect to hydrophobic cationic complexes. This situation (with allowance for the solubility of the background salts) explains why lithium or sodium perchlorates are most frequently used as inert salts in the study of OSC formed by aquoammine, ethylenediamine, and similar hydrophilic complexes. Sodium or potassium fluorides are chosen as inert salts in the study of the OSC of tris(2,2'-bipyridyl), tris(1,10-phenanthroline), and other hydrophobic compounds.

It is of interest to compare the association constants of a number of inert cationic complexes with the perchlorate ion, which is most widely used as inert anion.

The data in Table 1 show that for most cationic complexes with a charge of 1–4, the values of the logarithms of the stability constants of the perchlorate associates are ≥ 1. Increase in the size of the cationic complexes, for example in the series hexammine-, tris(ethylenediamine)-, and tris-(propylenediamine)cobalt(III), leads to a slight decrease in the stability constants (Table 1). A similar change is observed on going from tris(ethylenediamine)cobalt(III) to

tris(ethylenediamine)rhodium(III) or from *trans*-dichlorobis-(ethylenediamine)rhodium(III) to *trans*-dichlorobis(ethylenediamine)iridium(III). On the other hand, for the hydrophobic tris(2,2'-bipyridyl) and tris(1,10-phenanthroline) compounds, the change from iron(II) to ruthenium(II) and osmium(II) leads to an increase in the stability of the perchlorate associates.

Table 1. Logarithms of the association constants of transition metal complexes with the perchlorate ion at 298 K.

Cation	Medium	Method	lg β_1	Refs.
$[Co(en)_2(bipy)]^{3+}$	→0	S	1.66±0.05	[30]
$[Co(NH_3)_6]^{3+}$	→0	El	1.40±0.05	[31—33]
$[Co(NH_3)_6]^{3+}$	0	S	1.47	[34]
$[Co(NH_3)_6]^{3+}$	0	S	1.34	[35]
$[Co(NH_3)_6]^{3+}$	0.1 *M* $NaClO_4$	Sp	0.97	[36]
$[Co(en)_3]^{3+}$	→0	El	1.14±0.05	[32]
$[Co(en)_3]^{3+}$	0	El	1.18	[37]
$[Co(en)_3]^{3+}$	0	El	1.3	[38]
$[Co(en)_3]^{3+}$	1 *M* $NaClO_4$	Sp	—0.35	[39]
$[Co(pn)_3]^{3+}$	→0	El	1.08±0.05	[34]
$[Co(bipy)_3]^{3+}$	→0	S	2.10±0.05	[40]
$[Co(phen)_3]^{3+}$	→0	S	2.50±0.05	[40]
$[Co(NH_3)_5(H_2O)]^{3+}$	0	K	1.47	[41]
$[Co(NH_3)_5Cl]^{3+}$	0	S	1.15	[42]
$[Co(NH_3)_5(SO_4)]^{+}$	0	El	0.80	[43]
$[Co(en)_2(C_2O_4)]^{+}$	0	El	0.02±0.04	[44]
trans-$[Co(en)_2(SCN)Cl]^{+}$	→0	El	1.06±0.04	[45]
$[Rh(en)_3]^{3+}$	→0	El	0.93±0.05	[32]
trans-$[Rh(en)_2Cl_2]^{+}$	→0	El	1.08±0.05	[45]
trans-$[Ir(en)_2Cl_2]^{+}$	→0	El	1.00±0.04	[45]
$[Cr(NH_3)_6]^{3+}$	0	El	1.18±0.03	[46]
$[Cr(NH_3)_6]^{3+}$	0	Sp	1.00	[46]
$[Cr(en)_3]^{3+}$	0	El	1.04	[46]
$[Cr(en)_3]^{3+}$	0	El	1.31	[47]
$[Cr(en)_3]^{3+}$	0	Sp	1.21	[46]
$[Cr(en)_3]^{3+}$	0	Sp	0.90	[48]
$[Pt(NH_3)_6]^{4+}$	0	El	1.51±0.05	[49]
$[Pt(en)_3]^{4+}$	0	El	0.99±0.05	[49]
trans-$[Pt(en)_2Cl_2]^{2+}$	0	El	1.08±0.05	[45]
$[Fe(bipy)_3]^{2+}$	0	El	2.05±0.04	[50]
$[Fe(bipy)_3]^{2+}$	→0	S	2.05±0.05	[38]
$[Fe(bipy)_3]^{2+}$	0	E	2.08±0.06	[50]
$[Fe(phen)_3]^{2+}$	0	E	2.08±0.05	[50]
$[Fe(phen)_3]^{2+}$	→0	S	2.20±0.05	[51]
$[Fe(phen)_3]^{2+}$	0	E	2.13±0.06	[50]
trans-$[Fe(phen)_2(CN)_2]$	→0	S	0.59±0.03	[52]
$[Ru(bipy)_3]^{2+}$	0	El	2.38±0.05	[29]
$[Ru(bipy)_3]^{2+}$	→0	S	2.53±0.06	[29]
$[Ru(phen)_3]^{2+}$	0	El	3.18±0.05	[29]
$[Ru(phen)_3]^{2+}$	→0	S	3.45±0.07	[29]
$[Os(bipy)_3]^{2+}$	0	El	3.38±0.05	[29]
$[Os(bipy)_3]^{2+}$	→0	S	3.40±0.06	[29]
$[Os(phen)_3]^{2+}$	0	El	3.93±0.07	[29]
$[Os(phen)_3]^{2+}$	→0	S	4.32±0.05	[29]

Notation. Cations: en = ethylenediamine, pn = propylenediamine, bipy = 2,2'-bipyridyl, phen = 1,10-phenanthroline. Medium: →0 = extraction into an aqueous solution with zero ionic strength; 0 = recalculated analytically for $I = 0$. Methods: El = electrical conductivity measurement, S = solubility measurement, Sp = spectrophotometrically, K = study of the reaction kinetics, E = extraction.

Doubly-charged hydrophobic complexes[29,53–55] form more stable perchlorate associates than triply- and quadruply-charged hydrophilic cations (Table 1). The non-electrolyte *trans*-dicyanobis(1,10-phenanthroline)iron(II) tends to associate with the perchlorate ion. It should be particularly emphasised that a change in the charge of the coordination compound is not a decisive factor in the formation of perchlorate associates[54]. Many singly-charged cations have the same association constants with perchlorate ion as tris(ethylenediamine)cobalt(III). Judging from the values of the stability constants of the perchlorate associates of tris(ethylenediamine)- and haxamminecobalt(III), increase in the ionic strength of the solution leads to a decrease in the stability of the perchlorate associates (Table 1). The applicability of this regular feature is usually confirmed by published data[29,40,51,53,55], although in some cases there are exceptions [the perchlorate associates of tris(1,10-phenanthroline)-ruthenium(II) and iron(II)].

The ionic strength of the solution has practically no influence on the stability of the associates of coordination compounds with molecules[56,57] and neutral complexes with anions[54]. It should be noted that the values of the stability constants obtained at ionic strengths I which differ in magnitude and in the salts used to establish them can be extrapolated to $I = 0$ using Vasil'ev's equation[27]. This equation uses a distance of maximum approach of the ions equal to 4.9 Å. Change in this quantity over the range 3–6 Å, however, usually has little influence[26,58] on the values of the stability constants at $I = 0$.

Beginning from values of $I \leq 0.2$–0.3, the stability constants can be recalculated to $I = 0$ using Davies' equation[1], but in a number of cases[59–61] it does not lead to the same values as those obtained using Vasil'ev's equation.

Structural changes in the solvent and solvation processes in the second sphere have a significant influence on the formation of OSC in aqueous-organic solutions[62–65]. If the formation of OSC in aqueous solution is represented as the replacement of water molecules in the second sphere by an outer-sphere ligand

$$[MA_N](H_2O)_x(aq) + L(aq) \rightleftarrows [MA_N](H_2O)_yL(aq) + (x-y)H_2O \quad (1)$$

(M is the metal ion, A the inner-sphere ligands, and N their number), then the equilibrium constant of reaction (1) is related to the stability constant of the OSC by the relationship[64]:

$$\beta_e = \beta_1[H_2O]^{x-y} = \beta_1[H_2O]^z \quad (2)$$

Table 2. Logarithms of the stability constants lg β_1 of the outer-sphere complexes $[MA_N]SO_4$ and the equilibrium constants of reaction (1) lg β_e in aqueous methanol solutions at 298 K.[62,63]

MA_N	Methanol, mass %					
	0	10	20	30	40	50
$[Co(NH_3)_6]^{3+}$	3.48 6.97	3.54 6.94	3.68 6.98	3.79 6.97	3.91 6.95	4.08 6.96
$[Co(NH_3)_5Cl]^{2+}$	2.70 6.19	2.79 6.19	2.87 6.17	3.03 6.21	3.16 6.20	3.20 6.18
$[Fe(bipy)_3]^{2+}$	1.45 4.94	1.60 5.00	1.65 4.95	1.75 4.93	1.91 4.95	2.10 4.98

Note. The value of lg β_1 is given in the upper row, and the value of lg β_e in the lower row. The standard deviations for the values of lg β_1 are ±(0.03–0.05).

If equilibrium (1) does not break down in aqueous-organic solutions, and resolvation processes do not take place in the second sphere, it follows from the law of mass action that the role of the organic component often reduces to the role of a diluent of the water, and the correction $[H_2O]^z$ leads to a constant lg β_e in aqueous-organic solutions; z is an integer[64]. For sulphate OSC of hydrophilic and hydrophobic cationic complexes, the introduction of methanol, ethanol,

propanol, acetone, dioxan, and other solvents up to a concentration of 40–50 mass % does not change the values of $\lg \beta_e$ for $z = 2$. For the halide OSC of tris(ethylenediamine)cobalt(III),[65] the introduction of acetone up to 20 mass % does not change the values of $\lg \beta_e$.

Table 2 gives the stability constants in aqueous glycol solutions, where the correction $[H_2O]^z$ does not lead to constant values of $\lg \beta_e$. This case requires verification, since in the system being considered, the introduction of 20 mass % ethylene glycol lowers the value of the stability constant, and at higher ethylene glycol concentrations it increases. To date, this form of dependence of the values of the stability constants on the concentration of the organic component has been noted[66] only for this system. Moreoever, this effect is not observed for sulphate OSC of nitropentamminecobalt(III) in aqueous ethylene glycol solutions (Table 3). Additional verification of this idea for OSC with highly-charged anions, and also extension of the range of solvents and cationic complexes with different charge, containing inner-sphere ligands of different character, are required.

In some systems[67], the replacement of even 80% of water by methanol does not lead to a change in the constant β_e. This indicates the predominant role of the dilution factor.

Table 3. Logarithms of the stability constants[66,67] $\lg \beta_1$ and the equilibrium constants for reaction (1) $\lg \beta_e$ [62,63] for monosulphate OSC of tris(1,10-phenanthroline)iron(II) in aqueous methanol and aqueous ethylene glycol solutions at 298 K.

Solvent	Alcohol, mass %				
	0	20	40	60	80
Methanol	1.54 5.03	1.79 5.08	2.08 5.12	2.45 5.13	2.94 5.12
Ethylene glycol	1.71 5.20	1.59 4.88	1.86 4.90	1.98 4.66	2.36 4.44
Ethylene glycol*	2.55 6.04	2.77 6.04	3.03 6.06	— —	— —

*The data are given for the complex $[Co(NH_3)_5(NO_2)]SO_4$.
Note. See footnote to Table 2.

II. METHODS FOR DETERMINING THE CHANGES IN THERMODYNAMIC FUNCTIONS FOR THE FORMATION OF OUTER SPHERE COMPLEXES IN SOLUTION

The ultimate aim of the study of equilibria in solutions is the determination of the stoichiometry of the forms produced, and the calculation of stability constants and the changes in the thermodynamic functions (enthalpy, entropy, etc.) on complex formation[68]. From these viewpoints it is necessary, in the study of OSC, to establish the stoichiometry of the forms produced by the coordinatively-saturated complex $[MA_N]$ (N is the limiting coordination number) and the outer-sphere ligand L (anion or molecule). This problem is solved by the analysis and mathematical treatment of relationships of the type: solution property–solution composition. For the quantitative solution of this problem it is necessary to establish, in explicit, implicit, or parametric form, the functional relationship between the measured physicochemical property of the solution as a whole and its analytical composition. This functional relationship is established using three fundamental physicochemical concepts, given mathematically[68] by: 1) the material balance equations, 2) the equations of the law of mass action, and 3) equations relating a measured property of the solution as a whole, the partial contributions to this property from the individual chemical forms, and the equilibrium concentrations of these forms.

When an OSC with stoichiometry $[MA_N]L_m$ is formed in solution, the corresponding material balance equations have the form:

$$C_M = \{[MA_N]\} + \sum_m \{[MA_N]L_m\} \quad (3)$$

$$C_L = \{L\} + \sum_m m\{[MA_N]L_m\} \quad (4)$$

where c_M and c_L are the total (analytical) concentrations of the coordination compound $[MA_N]$ and the outer-sphere ligand L.

For the formation of OSC according to Eqn.(1), the corresponding equations of the law of mass action will be

$$\beta_1 = \{[MA_N]L\}/\{[MA_N]\} \cdot \{L\} \quad (5)$$

where β_1 is the concentration stability constant, which depends on temperature, pressure, the chemical character of $[MA_N]$ and L, and the nature of the forming medium. The concentration constant becomes constant if the conditions of a constant ionic medium with respect to the participants of the process being studied are observed [reaction (1)].[68]

The third group of equations is determined by the physicochemical method of study used.

The heats of formation of OSC in solution have been determined using a double differential microcalorimeter with a sensitivity of $(5.52 \pm 0.12) \times 10^{-3}$ J and a cell volume of 10 cm^3. The measurements were made by thermometric titration[59]. The complex compounds were synthesised by the usual methods, and analysed for the metal, hydrogen, carbon, nitrogen, and halogen. The difference between the observed and calculated concentration of the components determined did not exceed 0.5 abs.%. The purity of the synthesised and recrystallised specimens was verified from the published absorption spectra. The salt solutions used in the experiments were prepared from the "analytically pure" or "chemically pure" grade reagents, purified by recrystallising two or three times from water.

The heats of mixing of solutions containing $[MA_N]$ and the background electrolyte $[M'\Phi]$ at I = const with solutions of salts of the outer-sphere ligand M'L were measured. The heats of mixing of $M'\Phi$ with M'L were measured separately in additional experiments.

The heat of complex formation (Q) is related to the enthalpy change (ΔH_m^0) for the formation of the species $[MA_N]L_m$ by the expression

$$Q = V \sum_m \Delta H_m^0 \{[MA_N]L_m\} \quad (6)$$

where V is the volume of the solution, and $\{[MA_N]L_m\}$ represents the equilibrium concentrations of the forms $[MA_N]L_m$.

Eqns.(3)–(5) lead to the equation

$$\frac{Q}{V \cdot c_M} = \sum_m \frac{\Delta H_m^0 \beta_m \{L\}^m}{\left(1 + \sum_m \beta_m \{L\}^m\right)} \quad (7)$$

In most of the systems studied, the stoichiometry of the OSC formed and the values of the stability constants obtained from the results of independent methods of study (for example potentiometry, spectrophotometry, solubility, etc.) have

been used. The values of the stability constants were used to calculate the corresponding enthalpy changes for the formation of OSC from Eqn.(7). In a number of cases, the calculation of ΔH_1^0 and β_1 for single-ligand OSC have been carried out directly from thermochemical data[68].

The values of the free energy changes were calculated from the relationship[68]:

$$\Delta G_i^0 = -RT \ln \beta_i \ . \qquad (8)$$

The corresponding entropy changes for the formation of the OSC were calculated from the equation[68]:

$$\Delta G_i^0 = \Delta H_i^0 - T\Delta S_i^0 . \qquad (9)$$

The values of the changes in the thermodynamic functions are given with their uncertainties in the form of the standard deviations (see Tables 4–12). The results were treated by the least-squares method with allowance for the difference in the accuracy of the experimental data by introducing appropriate statistical weights[68], reflecting the estimates of the dispersions of the results on the measurement of the values of the heat.

III. OUTER-SPHERE COMPLEXES OF COBALT(III)

The outer-sphere complexes of cobalt(III) and the thermodynamics of their formation have been studied in most detail. A review of the study of OSC of cobalt(III) was published in 1970.[5] At that time, however, thermochemical measurements had been carried out for the formation of only the OSC of tris(ethylenediamine)cobalt(III). The studies were carried out in 3.0 M solutions of sodium or lithium perchlorate. The standard state indicated was used[67–77] in thermochemical studies of OSC up to 1975, when the first thermochemical studies[78–80] in dilute solutions with extrapolation of the thermodynamic data to aqueous solutions with zero ionic strength were published. Since 1975, thermochemical studies of the thermodynamics of formation have been carried out in solutions with ionic strengths of 0.1, 0.2, 0.3, 0.4, 0.5, and sometimes 0.75 and 1.0 [26,45,78–94] for the compounds of hexammine-,[79] tris(ethylenediamine)-,[79,81,83] tris(propylenediamine)-,[79] tris(2,2′-bipyridyl)-,[93] tris(1,10-phenanthroline)-,[94] chloro-,[80,87] bromo-,[80,85] nitro-,[80,85] sulphato-,[80,85], acetato-,[82,85] pentamminecarbonato-,[76] oxalato-,[92] malato-,[92] succinato-,[92] phthalato-,[92] tetrammine-, bis(acetylacetonato)-(ethylediamine)-,[88] and acetylacetonato, bis(ethylenediamine)-cobalt(III) [45] with sulphate, thiosulphate, sulphite, selenite, tellurite, and carbonate ions.

The thermochemical method has been used to study halide, thiocyanate, nitrate, carboxylate, and other OSC of cobalt(III). These measurements were made[93–102] in solutions with an ionic strength $I = 3$, maintained by adding sodium or lithium perchlorate.

The enthalpy changes for the formation of the OSC of cobalt(III) have usually been calculated[78–102] using the stability constants of the OSC, determined from potentiometric, solubility, spectrophotometric, and other data.

To illustrate ideas developed below, a small fraction of the data on the thermodynamics of the formation of OSC of cobalt(III) is given in Tables 4–8. Table 4 shows that in aqueous solutions with zero ionic strength, tris(ethylenediamine)-cobalt(III) forms mono- and bis(ligand) OSC with positive values of the entropy change. The enthalpy changes in these processes are small, and lie in the range ±2 kJ mole^{-1}. The differences between the stabilities of the OSC of tris-(ethylenediamine)cobalt(III) with different doubly-charged ligands are slight (Table 4); only the carbonate ion forms comparatively less stable OSC. A regular decrease in the stability constants and the positive values of the entropy changes is observed with increase in the serial number of the added ligand. The entropy changes are ~57–58 J mole^{-1} K^{-1} for the formation of mono-ligand OSC, and ~34 J mole^{-1} K^{-1} for the formation of bis(ligand) OSC.

Table 4. Values of the changes in the consecutive thermodynamic functions for the formation of OSC of tris(ethylenediamine)cobalt(III) at 298 K in aqueous solutions with zero ionic strength[79,103,104].

Ligand	n	$\lg K_n^0$	$\approx\Delta H_n^0$, kJ mole^{-1}	ΔS_n^0, J mole^{-1}K^{-1}
SO_4^{2-}	1	3.40 (3.30)	2.1	56
SO_4^{2-}	2	2.00 (1.80)	1.0	31
$S_2O_3^{2-}$	1	3.40	2.1	57
$S_2O_3^{2-}$	2	1.90	0.8	34
SO_3^{2-}	1	3.40	2.1	59
SO_3^{2-}	2	1.90	—0.8	34
SeO_3^{2-}	1	3.46	2.1	59
SeO_3^{2-}	2	1.85	—0.8	34
TeO_3^{2-}	1	3.32	2.1	59
TeO_3^{2-}	2	1.65	—0.8	34
CO_3^{2-}	1	2.90	1.0	57
CO_3^{2-}	2	1.65	2.9	21
$[Co(NH_3)_4C_2H_2(COO)_2]^+$	1	2.56	5.0	65
$[Co(NH_3)_4C_2H_2(COO)_2]^+$	2	1.40	5.4	38
$[Co(NH_3)_4C_2H_4(COO)_2]^+$	1	2.56	3.4	61
$[Co(NH_3)_4C_2H_4(COO)_2]^+$	2	1.30	2.9	34
$[Co(NH_3)_4C_6H_4(COO)_2]^+$	1	2.42	4.2	61
$[Co(NH_3)_4C_6H_4(COO)_2]^+$	2	1.15	2.1	29

Note. The standard deviations in the determination of the values of $\lg K_n^0$ are ±0.05 for $n = 1$ and $n = 7$, ±(0.07–0.12) for $n = 2$, ±(0.4–0.8) kJ mole^{-1} for ΔH_n^0, and ±(2–3) J mole^{-1} K^{-1} for ΔS_n^0. The improved values[79] used to calculate the enthalpy and entropy changes for the OSC are given in brackets.

Table 5. Values of the changes in the thermodynamic functions for the formation of sulphate OSC of coordination compounds of cobalt(III) at 298 K in aqueous solutions with zero ionic strength[76,79,80,82,92,103].

Cation	n	$\lg K_n^0$	ΔH_n^0, kJ mole^{-1}	ΔS_n^0, J mole^{-1}K^{-1}
$[Co(NH_3)_6]^{3+}$	1	3.40	—2.1	59
$[Co(en)_3]^{3+}$	1	3.30	—2.1	56
$[Co(en)_3]^{3+}$	2	1.80	—1.0	31
$[Co(ph)_3]^{3+}$	1	3.22	—2.5	54
$[Co(ph)_3]^{3+}$	2	1.80	—1.5	30
$[Co(NH_3)_5Cl]^{2+}$	1	2.87	3.6	67
$[Co(NH_3)_5Cl]^{2+}$	2	1.45	0	28
$[Co(NH_3)_5Br]^{2+}$	1	2.80	2.9	64
$[Co(NH_3)_5Br]^{2+}$	2	1.17	1.9	29
$[Co(NH_3)_5(NO_2)]^{2+}$	1	2.88	3.4	67
$[Co(NH_3)_5(NO_2)]^{2+}$	2	1.30	2.1	32
$[Co(NH_3)_5(CH_3COO)]^{2+}$	1	2.80	1.5	59
$[Co(NH_3)_5(CH_3COO)]^{2+}$	2	1.40	1.3	31
$[Co(NH_3)_5(SO_4)]^{+}$	1	2.42	6.3	67
$[Co(NH_3)_5(SO_4)]^{+}$	2	0.60	4.2	25
$[Co(NH_3)_4(CO_3)]^{+}$	1	2.35	5.0	61
$[Co(NH_3)_4(CO_3)]^{+}$	2	0.80	3.4	27
$[Co(NH_3)_4(C_2O_4)]^{+}$	1	2.35	5.0	59
$[Co(NH_3)_4(C_2O_4)]^{+}$	2	1.15	2.9	31

The data in Table 5 show that the stability of the sulphate OSC tends to decrease in the cationic complex order: hexammine- > tris(ethylenediamine)- > tris(propylenediamine)-cobalt(III); there is a slight decrease in the contribution of the entropy component to the free energy change. The

decrease in these quantities is small, however, and lies at the error limit in the determination of the thermodynamic parameters.

Table 6. Values of the changes in the thermodynamic functions for the formation of the monosulphate OSC $[Co(en)_x \cdot (acac)_{3-x}]$ at 298 K and different ionic strengths, maintained using sodium perchlorate and sulphate[88].

I	$\lg \beta_1$	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}	I	$\lg \beta_1$	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}
	$[Co(en)_2(acac)]^{2+}$				$[Co(en)(acac)_2]^+$		
0	2.49	0.4	46	0	2.05	0.4	38
0.3	1.10	4.2	34	0.3	1.10	2.5	29
0.5	0.80	5.4	34	0.5	0.70	3.8	25
1.0	0.07	8.4	29	1.0	0.22	5.0	21

Note. The standard deviations in the determination of the values of lg β_1 are ±(0.03–0.05); ±(0.4–0.8) kJ mole^{-1} for ΔH_1^0; and ±(2–3) J mole^{-1} K^{-1} for ΔS_1^0.

Table 7. Values of the changes in the thermodynamic functions for the formation of the sulphate OSC of tris(2,2′-bipyridyl)- and tris(1,10-phenanthroline)cobalt(III) at 298 K and different ionic strengths[93,94].

I	$-\Delta G_1^0$, kJ mole^{-1}	$-\Delta H_1^0$, kJ mole^{-1}	$-\Delta S_1^0$, J mole^{-1}K^{-1}
	phen		
0	13.0	23	34
0.1	6.3	24	59
0.25	3.7	30.5	59
0.5	2.2	35.5	112
0.75	1.1	42.6	139
	bipy		
0	14.2	25.9 26.4	75
0.1	7.0(5.7)	27.6 43.5	69
0.25	4.55(5.2)	31.4 25.5	90 (67)
0.5	2.7(2.65)	43.1 43.9	134 138
0.75	1.6(1.1)	43.1 53.6	138 176
{0	{13.3}	{29.7}	{54}

Note. The standard deviations of the determinations are ±(0.4–0.6) kJ mole^{-1} for ΔG_1^0; ±(0.8–0.6) kJ mole^{-1} for ΔH_1^0; and ±(3–20) J mole^{-1} K^{-1} for ΔS_1^0.

The values are given for a combination of potentiometric and thermochemical methods; the values in round brackets correspond to purely thermochemical data, and those in braces were obtained by the electrical conductivity method at 293–318 K.

For hydrophilic cationic complexes, the change from the hexammine- [tris(diamine)-] to acidopentammine- and then acidotetramminecobalt(III) leads to a marked decrease in the stability of the OSC with doubly-charged ligands. This decrease in the stability of OSC with decrease in the charge of the central group is accompanied by a regular increase in the positive contribution of the enthalpy component, and is clearly observed for monoligand OSC (Table 5).

The differences in the stability of OSC formed by different acidopentammines of cobalt(III) lie just beyond the error limits in the determination of the changes in the thermodynamic functions (see Table 5). Similar conclusions can be reached about the stability of the OSC of acidotetramminecobalt(III) compounds (Table 5). Sulphatopentamminecobalt(III) forms outer-sphere complexes with stabilities close to those of acidotetrammines of cobalt(III), due to the fact that these complexes have the same charge of +1. The date in Table 5 indicate that the entropy changes are 63 ± 8 J mole^{-1} K^{-1} for the formation of the monoligand OSC of cobalt(III) ammines, and 29 ± 8 J mole^{-1} K^{-1} for the formation of the bis(ligand) OSC.

Table 8. Values of the enthalpy and entropy changes for the formation of associates of amines with coordination compounds of cobalt(III) in aqueous lithium perchlorate or chloride solutions at 298 K.[105]

Cation	L	Medium	$-\Delta H_1^0$, kJ mole^{-1}	$-\Delta S_1^0$, J mole^{-1}K^{-1}
$[Co(NH_3)_6]^{3+}$	NH_3	3 *M* LiCl	4.2	25
$[Co(NH_3)_6]^{3+}$	NH_3	0.2 *M* $LiClO_4$	3.8	21
$[Co(en)_3]^{3+}$	en	3.0 *M* $LiClO_4$	27.6	113
$[Co(en)_3]^{3+}$	en	3 *M* LiCl	29.0	109
$[Co(en)_3]^{3+}$	py	3 *M* $LiClO_4$	18.4	92
$[Co(en)_3]^{3+}$	NH_3	3 *M* LiCl	8.4	42
$[Co(en)_3]^{3+}$	CH_3NH_2	3 *M* $LiClO_4$	12.5	63
$[Co(NH_3)_5(HCOO)]^{2+}$	NH_3	3 *M* $LiClO_4$	9.6	38

Note. The standard deviations of the determinations are ±(0.8–2.0) kJ mole^{-1} for ΔH_1^0, and ±(3–8) J mole^{-1} K^{-1} for ΔS_1^0.

Similar entropy changes are characteristic of the addition of various other doubly-charged anions[78–87,91,92]. The results of Refs. 32, 34, and 105–112 were obtained from the temperature dependence of the stability constants of only single-ligand OSC, and most of them confirm the conclusion that the entropy change has the practically constant value given above. Analysis of the data in Ref. 111 shows that the enthalpy change for the formation of monohydrogen phosphate OSC of tris(ethyldiamine)cobalt(III) is close to zero, and calculation of the entropy changes gives a value of 63 J mole^{-1} K^{-1}. A study of the association of tris(biguanidine)cobalt(III) with the sulphate ion at 298 K and 308 K[112] showed that the entropy changes for the formation of monoligand OSC are 59 J mole^{-1} K^{-1}. With the assumption that temperature does not influence the stability constant of the mono-oxalato-complex of hexamminecobalt(III),[32,34] we obtain entropy changes of 63 J mole^{-1} K^{-1}. Chloropentamminecobalt(III), even with the quadruply-charged pyrophosphate ion, forms OSC whose entropy changes at 293 K and an ionic strength of 0.1 are 70 J mole^{-1} K^{-1}.[23]

In a number of cases, the formation of OSC in which the number of added ligands is three has been detected[78–102]. The small values of the changes in the thermodynamic functions, however, together with the large errors in their determination and the possibility of a contribution from changes in the activity coefficients, make an unambiguous quantitative discussion of the regular features of the formation of these OSC impossible[113,114].

It is of interest to compare the data of the present authors[80] on the thermodynamics of the formation of OSC of cobalt(III) with published data[114,115] obtained for monoligand complexes from kinetic and sometimes spectrophotometric studies.

The dependence of the acid hydrolysis constant on the sulphate ion concentration for chloropentamminecobalt(III) at an ionic strength of 0.3 and temperatures of 313–328 K [115] made

it possible to determine the association constant, equal to 32.5, and $\Delta G_1^0 = -9.2$ kJ mole^{-1}, $\Delta H_1^0 = -17.2$ kJ mole^{-1}, and $\Delta S_1^0 = -26$ J mole^{-1} K^{-1}. The direct determination of these parameters from potentiometric and thermochemical data[80] gave values of the above functions equal to 14, -8.2 kJ mole^{-1}, 6.3 kJ mole^{-1}, and 48.5 J mole^{-1} K^{-1} respectively. Comparison of the direct and indirect data on the enthalpy and entropy changes for the formation of the sulphate associate of chloropentamminecobalt(III) shows differences even in the signs of these functions.

Doubt must be cast on the values obtained from the kinetic data[115], and also on the published thermodynamic characteristics[116] of the malate and phthalate OSC of chloropentamminecobalt(III). Contrary to the data of Ref.116, these monoligand OSC should be formed with positive enthalpy and entropy changes. The enthalpy and entropy changes at 313 K in 0.3 M sodium perchlorate solutions, however, are respectively -25 kJ mole^{-1} and -53 J mole^{-1} K^{-1} for the malate OSC, and -27 kJ mole^{-1} and -58 J mole^{-1} K^{-1} for the phthalate OSC of chloropentamminecobalt(III).[116] The values of the enthalpy and entropy changes for the formation of phthalate OSC of aquopentamminecobalt(III) in solutions with an ionic strength of 0.3 at 323 K, equal to 24 kJ mole^{-1} and 100 kJ mole^{-1}, obtained[117] from the temperature dependence of the association constants, appear more correct. The latter were determined from the dependence of the rate constants of inner-sphere ligand replacement on the concentration of the outer-sphere ligand.

Since the dependence of the rate constants of hydrolysis, inner-sphere ligand replacement, etc. on the concentration of the outer-sphere ligand is non-linear, the determination of the stability constants of the resulting OSC from kinetic data is difficult, and associated with appreciable errors[118]. In most cases, the influence of temperature on the stability constants of the OSC is weak[119,120], and it is not possible to determine the enthalpy and entropy components of the free energy change.

The successive replacement of ethylenediamine by acetylacetone in the inner sphere of cobalt(III) leads (Tables 5 and 6) to a decreased stability of the monosulphate OSC. The positive contribution of the entropy component tends to get smaller with increase in the number of acetylacetone molecules in the inner sphere of cobalt(III). Published ideas on the reasons for this decrease are contradictory[45]. The decrease in the stability of the hydrate layer[47] and the increase in the donor–acceptor interaction with the π-system of the acetylacetone molecules with an increase in their number in the inner sphere represent[121] equally weighty arguments explaining the decrease in the contribution of ΔS_1^0 to ΔG_1^0.

The formation of monosulphate OSC by the hydrophobic tris(2,2′-bipyridyl)cobalt(III) and tris(1,10-phenanthroline)-cobalt(III), unlike the formation of OSC by hydrophilic cations (Tables 4 and 5), takes place with negative values of the enthalpy and entropy changes (Table 7). The absence of acidic protons, the hydrophobic character of the inner-sphere ligands, and the formation of π-bonds between M and phen (bipy) suggest that the solvation of these cations is determined by the dipole moment of the solvent and van der Waals interaction[93,94].

The reaction of tris(2,2′-bipyridyl)- and tris(1,10-phenanthroline)cobalt(III) with a solvent is determined by the strong hydrophobic character of 1,10-phenanthroline and 2,2′-bipyridyl.[122] The large size of the cationic complexes and the shielding of the central metal ion by the inner-sphere ligands, which form $\pi(M \rightarrow Am)$ bonds, where Am = bipy or phen, weaken the electrostriction interaction of the cationic complex with the solvent molecules. With ion-dipole and van der Waals interactions of the solvent with coordination compounds, hydrophobic hydration may take place[123]. In this case, large ionic complexes such as tris(1,10-phenanthroline)-cobalt(III) do not have a primary hydrate layer, and the influence of their secondary hydration is revealed chiefly in the effect on the structure of water layers adjoining the ions, which increases the degree of ordering. It must be assumed that the formation of associates in this case is accompanied by the combination of the cavities in which the ions are situated, or by the replacement of solvent molecules by the outer-sphere ligand in the secondary hydrate layer. Processes of this kind should not lead to the extensive desolvation processes in the case of highly charged hydrated ions which are observed in the outer-sphere association of sulphate ions with tris(1,10-phenanthroline)cobalt(III), where in contrast to the outer-sphere association of hydrophilic amine compounds of cobalt(III) their formation is accompanied by appreciable negative enthalpy and entropy changes (Tables 4–7).

The data in Tables 4–7 and Refs.14 and 79–94 show unambiguously that the nature of the interaction of coordination compounds with a solvent plays a predominant role in the formation of outer-sphere complexes. Ahrland's criterion[124] for the thermodynamic determination of the type of complex (inner- or outer-sphere) in labile systems is not general; its applicability is restricted to hydrophilic systems, and it cannot be used in hydrophobic systems[93,94].

Thermochemical studies of the reaction of cationic cobalt(III) complexes with amines in the outer sphere are complicated[62] by the high values of the heats of mixing of the solutions of the background electrolytes with amines. For this reason, the thermodynamics of the formation of OSC with amines has been studied[105] only from the temperature dependence of the stability constants of the OSC. The values of the enthalpy and entropy changes obtained in this way are naturally approximate. The quantitative data obtained (Table 8) indicate, however, that the addition of ammonia, ethylenediamine, and pyridine to hexamminecobalt(III) and also to tris(ethylenediamine)- and acetatopentamminecobalt(III) is accompanied by negative enthalpy and entropy changes. The addition of ethylenediamine and pyridine is accompanied by negative enthalpy and entropy changes of greater absolute magnitude than the addition of ammonia (Table 8). The ratio of the thermodynamic functions indicated above is due to the greater complexity of the structures of ethylenediamine and pyridine compared with ammonia.

Published data[26,76,79,81–83,92–94] make it possible to analyse the nature of the influence of the ionic strength of the solution on the formation of OSC. In all the systems examined, except the OSC of tris(2,2′-bipyridyl)- and tris(1,10-phenanthroline)cobalt(III), the ionic strength was maintained using sodium perchlorate. Increase in the concentration of this salt (that is in the ionic strength of the solution) decreases the values of the stability constants of the OSC. This decrease takes place as far as saturated sodium perchlorate solutions, and is due to the association of the cationic complexes with the perchlorate ion. The quantitative characteristics of the first stage of this association were examined in the previous section of the present review.

The contributions of the enthalpy and entropy components of the free energy changes vary in different ways with increase in the ionic strength of the solution for cationic complexes with different charges. In most cases, a decrease in the stability of the OSC of the tris(diamine)-compounds of cobalt(III) accompanies a decrease in the entropy component of the free energy changes at $I = 0$–0.5. The change from $I = 0.5$ to $I = 3.0$ leads to a further decrease in the stability of the OSC with an increase in the endothermicity of OSC formation[26,79,81–83].

For the doubly-charged cationic complexes, for example acidopentamminecobalt(III), and also for the singly-charged sulphatopentammine- and carboxylatotetramminecobalt(III), a decrease in the stability of the OSC is observed with increase in the ionic strength of the solution and the simultaneous increase in the positive enthalpy changes for the formation of the OSC.[26,76,92].

For the mixed coordination compounds $[M(en)_x(acac)_{3-x}]$, increase in the ionic strength of the solution leads to an increase in the positive enthalpy changes and to smaller positive values of the entropy change (Table 6). Increase in the ionic strength of the solution, maintained using sodium fluoride, leads to a decrease in the stability of the OSC of tris(2,2'-bipyridyl)cobalt(III), and also tris(1,10-phenanthroline)cobalt(III), and the absolute values of the negative enthalpy and entropy for the formation of the OSC increase[26, 93,94]. The influence of the ionic strength of the solution on the thermodynamic functions for the formation of the OSC is due to the association of the cationic complexes with the ions of the background electrolyte, and also to the dehydrating influence of the added electrolyte.

Table 9. Changes in the thermodynamic functions for the formation of monoligand OSC of the tris(ethylenediamine) compounds of chromium(III), rhodium(III), iridium(III), ruthenium(III), and platinum(IV) in solutions with $I = 0$ at 298 K.[29,45,78,84,91,125–128]

L	$-\Delta G_1^0$, kJ mole^{-1}	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}
	Cr(III)		
$S_2O_3^{2-}$	19.3 (18.8)	—2.4 (—2.5)	57 (63)
SO_3^{2-}	18.6 (18.4)	—2.3 (—2.3)	56 (55)
SeO_3^{2-}	18.3 (18.0)	1.7 (1.7)	67 (66)
TeO_3^{2-}	18.0 (17.6)	1.4 (1.0)	65 (63)
SO_4^{2-}	17.8 (17.2)	0 (0)	59 (59)
CO_3^{2-}	18.0 (18.0)	1.2 (0.8)	64 (63)
	Rh(III)		
$S_2O_3^{2-}$	20.1 (14.9)	—2.2 (3.4)	60 (61)
SO_3^{2-}	19.3	—2.3	58
SeO_3^{2-}	18.8 (14.9)	—1.7 (7.1)	69 (73)
TeO_3^{2-}	18.8 (14.4)	—1.3 (5.9)	67 (67)
SO_4^{2-}	18.0 (16.5)	0.2 (4.6)	65 (71)
CO_3^{2-}	18.4	0.9	61
	Ir(III)		
$S_2O_3^{2-}$	19.9	—0.8	59
SO_3^{2-}	18.8	1.3	59
SeO_3^{2-}	18.8	—0.4	62
TeO_3^{2-}	18.4	2.1	69
SO_4^{2-}	18.0	—0.8	59
CO_3^{2-}	18.7	2.5	71
	Ru(III)		
$S_2O_3^{2-}$	17.7 (15.9)	—1.3 (4.0)	55 (66)
SO_3^{2-}	17.3 (14.7)	—0.4 (2.1)	56 (58)
SeO_3^{2-}	17.1 (15.9)	—0.4 (6.7)	56 (76)
SO_4^{2-}	17.1 (16.7)	—0.4 (8.4)	56 (84)
	Pt(IV)		
SO_4^{2-}	22.6	—0.4	76
SO_3^{2-}	26.0	—0.8	84

Note. The standard deviations of the determinations are ±(0.3–0.6) kJ mole^{-1} for ΔG_1^0; ±(0.4–0.8) kJ mole^{-1} for ΔH_1^0; and ±(2–4) J mole^{-1} K^{-1} for ΔS_1^0. The data in brackets for Cr(III) are for the OSC of tris(propylenediamine)chromium(III),[91] for Rh(III) they are for the OSC of chloropentamminerhodium(III),[28] and for Ru(III) they are for the OSC of chloropentammineruthenium(III).[31]

IV. OUTER-SPHERE COMPLEXES OF RHODIUM(III), IRIDIUM(III), PLATINUM(IV), AND CHROMIUM(III)

The study of the thermodynamics of the formation of OSC by rhodium(III), iridium(III), platinum(IV), and chromium(III) cations using the thermochemical method and extrapolation of the thermodynamic functions to aqueous solutions with zero ionic strength has been much less extensive than that for the corresponding cobalt(III) compounds. The formation of OSC by the tris(ethylenediamine) compounds of all these metals has been studied[45,78,84,92,125–127]; in addition, the formation of OSC with the chloropentammines has been studied for rhodium(III) [90,128] and platinum(IV),[45,86,89] with the tris(propylenediamine) compound for chromium(III),[91] and for the *trans*-dichlorobis(ethylenediamine) compounds for rhodium(III), iridium(III), and platinum(IV).[45] As with the cobalt(III) complexes, the outer-sphere ligands used were the sulphate, thiosulphate, sulphite, selenite, tellurite, and carbonate ions. The reaction of hydroxopentammineplatinum(IV) with chloride and bromide ions has been studied[45,89]. The OSC complexes of hexammine- and tris(1,10-phenanthroline)chromium(III) with sulphate ions have been studied[129,130] at different temperatures by the electrical conductivity method. Some of the data on the thermodynamics of the formation of the OSC of rhodium(III), iridium(III), platinum(IV), and chromium(III) are given in Tables 9–11.

Table 10. Changes in the thermodynamic functions for the formation of monohalide OSC of platinum(IV) in solutions with zero ionic strength at 298 K.[45,86,89]

Cation	L	$-\Delta G_1^0$, kJ mole^{-1}	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}
$[Pt(en)_3]^{4+}$	Cl^-	9.2	6.3	50
$[Pt(en)_3]^{4+}$	Br^-	8.8	11.7	67
$[Pt(NH_3)_5Cl]^{3+}$	Cl^-	9.2	0.4	34
$[Pt(NH_3)_5Cl]^{3+}$	Br^-	8.4	2.9	38
$[Pt(NH_3)_5(OH)]^{3+}$	Cl^-	8.8	2.9	38
$[Pt(NH_3)_5(OH)]^{3+}$	Br^-	8.0	4.0	40

Note. See footnote to Table 9.

Table 11. Changes in the thermodynamic functions for the formation of monosulphate OSC by *trans*-$[M(en)_2Cl_2]^{2+}$ ions in solutions with zero ionic strength at 298 K.[45]

M	$-\Delta G_1^0$, kJ mole^{-1}	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}
Co(III)(Co(en)$_2$(SCN)Cl$^+$)	13.0	6.3	63
Rh(III)	12.1	5.4	59
Ir(III)	10.9	3.8	46
Pt(IV)	15.1	5.0	67

Note. See footnote to Table 9.

The data in Tables 9 and 11 show that in aqueous solutions with zero ionic strength at 298 K, all the monoligand OSC with doubly-charged ligands studied are formed with small (less than ±8.4 kJ mole^{-1}) changes in the enthalpy, and positive values of the entropy changes, equal to 63 ± 8 J mole^{-1} K^{-1}. The values of the entropy changes for practically all the OSC of hydrophilic cationic complexes lie in this range. There are only a few systems in which the

entropy changes lie outside this range. They include the sulphate OSC of *trans*-dichlorobis(ethylenediamine)iridium-(III), where $\Delta S_1^0 = 46$ J mole^{-1} K^{-1},[45] and also the sulphate and sulphite OSC of tris(ethylenediamine)platinum(IV), where $\Delta S_1^0 = 76$ J mole^{-1} K^{-1} and 84 J mole^{-1} K^{-1} respectively[76,84]. It is not yet possible to say unambiguously whether these deviations are due to experimental error or to specific features of the formation of the OSC.

In most cases, in contrast to the OSC of amine compounds of cobalt(III), only the formation of monoligand associates by amine compounds of rhodium(III), iridium(III), platinum-(IV), and chromium(III) has been studied. Qualitative and semi-quantitative indications of the formation of multiligand complexes have been reported[29,78,84]. Attempts to determine the thermodynamic characteristics of the formation of even the bis(ligand) OSC of, for example, chromium(III),[78,84] rhodium(III),[78,84] or platinum(IV),[31] however, gave extremely rough or approximate values of the thermodynamic functions. It can only be assumed that the bis(ligand) associates are formed with approximately the same changes in the thermodynamic functions as the OSC of cobalt(III).

The stability of the monoligand OSC of tris(diamine) compounds of rhodium(III), iridium(III), chromium(III), and platinum(IV) decrease in the following order of doubly-charged anions: thiosulphate > sulphite > selenite > tellurite > sulphate ions (Tables 9–11). This is less characteristic of the OSC of amine compounds of cobalt(III). A deviation from the above order is observed for OSC of chloropentamminerhodium(III), where the sulphate associates are more stable than the thiosulphate.

The chloride and bromide associates of tris(ethylenediamine)-, and also chloro- and hydroxopentammineplatinum-(IV), are formed (Table 10) with positive values of the enthalpy and entropy changes. The enthalpy and entropy changes for the formation of the bromide OSC of platinum(IV) are positive and of larger magnitude than those for the formation of the chloride OSC (Table 10). Usually, in the series of "fluoride–iodide" OSC, the absolute magnitude of the entropy changes decrease[71,94], even taking negative values for bromide and iodide OSC,[51,99] and high positive values of the enthalpy and entropy changes are observed only for fluoride OSC.[94] This variation of the enthalpy and entropy changes in the halide ion series is due to hydration factors. The anomalous ratios of the enthalpy and entropy changes for the chloride and bromide OSC of amine compounds of platinum(IV)[45] require verification.

The formation of sulphate OSC of hexamminechromium(III) takes place at values of the enthalpy changes close to zero, and the entropy changes are 63 J mole^{-1} K^{-1}.[127] At the same time, tris(1,10-phenanthroline) chromium(III) adds on sulphate ion with negative values of the enthalpy and entropy changes[126], confirming the thermodynamic data for the corresponding OSC of hydrophilic and hydrophobic cobalt(III) cations (Tables 5 and 7).

On going from the tris(diamine) compounds to the acidopentammines, and then to the *trans*-dichloro- or chloro-(thiocyanato)- (Tables 9–11) -bis(ethylenediamine) compounds of cobalt(III), rhodium(III), and iridium(III), the stability of the OSC decreases in this order for cationic complexes, because of the decrease in the charge on the cationic complexes. The stability of the OSC increases significantly on going from the triply-charged cations of cobalt(III), rhodium(III), and iridium(III) to the quadruply-charged cations of platinum(IV) (Tables 9 and 11).

Interesting relationships are observed in the analysis of data on the stability of the OSC of chloropentammines of cobalt(III) and rhodium(III) (Table 9). The thiosulphate, selenite, and tellurite OSC of chloropentamminecobalt(III) are more stable than the corresponding rhodium(III) compounds. The thiosulphate, selenite, and tellurite ions can transfer charge to the antibonding orbitals of chloropentamminecobalt(III). As a consequence of the greater splitting of the *d* orbitals in the rhodium(III) complexes, the outer-sphere charge transfer in these compounds is less than that in the corresponding cobalt(III) compounds[90,94,130]. For the association of sulphate ions, the charge transfer is slight, because the stabilities of the OSC of the chloropentammines of cobalt(III) and rhodium(III) with the sulphate ion are practically identical.

For most hydrophilic cationic complexes of cobalt(III), rhodium(III), chromium(III), platinum(IV), and iridium(III),[79,81,83,84,123–130] increase in the ionic strength of the solution, maintained by sodium perchlorate, leads to a decrease in the stability of OSC with different ligands L; with increase in I, the positive contribution of the entropy changes decreases. For the sulphate and tellurite OSC of tris(ethylenediamine)-iridium(III), the positive values of the enthalpy changes increase with increase in the ionic strength of the solution.

It should be noted that the dependence of the enthalpy and entropy changes on the ionic strength of the solution is not unique even for the OSC of cationic complexes with similar properties, for example chloropentamminecobalt(III) and chloropentamminerhodium(III).[130] Further studies are necessary to determine the reasons for such marked differences in the changes in the thermodynamic functions.

Table 12. Changes in the thermodynamic functions for the formation of monoligand chloride and sulphate OSC of tris-(2,2′-bipyridyl) compounds of iron(II) and ruthenium(II) at 298 K in aqueous solutions with constant ionic strengths, maintained using sodium fluoride[31,55].

I	$-\Delta G_1^0$, kJ mole^{-1}	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}
	Fe(II),Cl$^-$		
0	7.1	4.0	37
0.25	3.6	4.8	28
0.50	2.3	5.4	26
0.75	1.3	6.1	25
	Ru(II), Cl$^-$		
0	11.6(11.5)	0	39
0.25	7.7(8.2)	0.6	28
0.50	6.6(7.6)	1.0	25
0.75	5.5(7.4)	1.0	22
	Ru(II), SO_4^{2-}		
0	12.8	—21.0	—29
0.25	6.4	—16.7	—38
0.5	5.3	—13.8	—29
0.75	4.4	—9.2	—25

Note. The standard deviations of the determinations are ±(0.3–0.5) kJ mole^{-1} for ΔG_1^0; ±(0.4–0.8) kJ mole^{-1} for ΔH_1^0; and ±(2–4) J mole^{-1} K^{-1} for ΔS_1^0. The data for the osmium(II) OSC are given in brackets.

V. OUTER-SPHERE COMPLEXES OF IRON(II), RUTHENIUM-(II), (III); AND OSMIUM(II)

At present, there are only isolated accurate data[34,131,132] on the thermodynamics of the formation of OSC by cationic complexes of iron(II) and ruthenium(II), (III), and information on the composition and stability constants of OSC of

osmium(II). The OSC of amine compounds of ruthenium(III) have been most fully studied by the thermochemical method[29]. Halide, perchlorate, sulphate, thiosulphate, sulphite, and selenite ions were used as outer-sphere ligands. Some of the data on the thermodynamics of the formation of these OSC are given in Tables 9 and 12.

The data in Table 12 and published data[29,53–55,57] indicate that the stability of the OSC of the tris(2,2′-bipyridyl) and tris(1,10-phenanthroline) compounds of iron(II), ruthenium(II), and osmium(II), in the great majority of cases, increases on going from Fe^{II} to Os^{II}; from the tris(2,2′-bipyridyl) to the tris(1,10-phenanthroline) complexes; and with change in the outer-sphere ligands in the order: chloride < bromide < iodide < perchlorate ions.

There is a linear correlation between lg β_1 and the heats of hydration of the outer-sphere ligands[29,31,33]

$$\lg\beta_1 = A + B\,\Delta H^0_{hydr}(L)$$

where A and B are constants for each cationic complex. For the OSC of iron(II), ruthenium(II), and osmium(II) studied, A lies in the range 3.4–8.5, and B in the range 0.018 to 0.062. A linear relationship is also observed between the value of lg β_1 and the reciprocal of the crystal-chemical radius (Goldschmidt) of the outer-sphere anion after allowing an empirical correction of 0.028 nm. The existence of these corrections indicates that in the association of hydrophobic cationic complexes, an important role is played by both electrostatic and hydration factors.

The stability of the above OSC decreases regularly with increase in the serial number of the added ligand. The published data[133,134] indicating deviations from this regular trend require verification. The increase in the stability of the chloride OSC in the order iron(II) < ruthenium(II) < osmium(II) is related to the decrease in the positive contribution of the enthalpy changes.

Studies by the present authors[55,131] have shown that the stability of the OSC depends to a much greater extent on the nature of the central metal ion when the inner sphere contains ligands forming π-bonds than when inner-sphere ligands forming only σ-bonds are present. In some systems (even when the inner sphere contains π-bonds), the differences in the stability of the OSC when, for example, ruthenium(II) is replaced by osmium(II) are small and disappear. This is indicated by the values of the free energy changes for the monochloride complexes of the tris(2,2′-bipyridyl) compounds of ruthenium(II) and osmium(II) in aqueous solutions with zero ionic strength, given in Table 12.

In general, the stability of monoligand OSC of tris(2,2′-bipyridyl) and tris(1,10-phenanthroline) complexes decreases in the following metal ion order: $Os^{II} > Ru^{II} > Co^{III} > Fe^{II}$. The tendency to form π-acceptor bonds increases from Fe^{II} to Os^{II}, that is in the order $3d^6 > 4d^6 > 5d^6$ ions. The hydrophobic properties of the cationic complexes increase in the order indicated, since the influence of the charge on the metal ion on the water molecules becomes weaker as it is shielded by ligands forming π-acceptor bonds. The position of Co^{III} in this series is explained by the decrease in the strength of the hydrophobic properties of the cationic complexes $[CoAm_3]^{3+}$, where Am = phen or bipy, compared with $[MAm_3]^{2+}$, where M = Ru^{II} or Os^{II}, and contradicts simple electrostatic ideas.

The greater stability of the OSC of tris(1,10-phenanthroline) complexes compared with tris(2,2′-bipyridyl) compounds is due to the more hydrophobic properties of 1,10-phenanthroline and the coplanar structure of the inner-sphere molecules of 2,2′-bipyridyl, which increases the size of the complexes $[M(bipy)_3]^{z+}$ compared with $[M(phen)_3]^{z+}$. This effect is not so marked for Co^{II} and Fe^{II}, but is appreciable for Ru^{II} and Os^{II}.

The order of the outer-sphere anions with respect to decreased stability of the OSC of hydrophobic cations is determined by the fact that a decrease in the heat of hydration and an increase in the size of the anions lead to an increase in their tendency to associate with hydrophobic cations. It must be assumed, however, that in these interactions, use is made of the structural cavities of the 2,2′-bipyridyl and 1,10-phenanthroline molecules coordinated to the cations, that is "hydrophobic packets". A number of experimental data[133,134], and also the fact that the maximum number of added ligands in the outer sphere is three[135,136], confirm this. For some tris(2,2′-bipyridyl) and tris(1,10-phenanthroline) complex systems, however, there are indications that a fourth ligand is attached. The question of the existence of these OSC remains open.

Sulphate OSC of tris(2,2′-bipyridyl)ruthenium(II) (Table 12), like the corresponding compounds of other hydrophobic cations, are formed with negative values of the enthalpy and entropy changes. In contrast to the case of the sulphate OSC of tris(2,2′-bipyridyl)cobalt(III), however, a sharp increase in the absolute magnitude of the negative values of the entropy changes is not observed with increase in the ionic strength of the solution.

Sulphate, thiosulphate, sulphite, and selenite OSC have been studied for a number of compounds of ruthenium(III). Tris(ethylenediamine)ruthenium(III) forms more stable OSC than chloropentammineruthenium(III), and this is explained by the charges of the cationic complexes (Table 9). As in the case of other coordination compounds of transition metals, the change from tris(ethylenediamine) OSC to chloropentammine OSC leads to an increase in the positive values of the enthalpy changes (Table 9). At zero ionic strength, OSC of chloropentammineruthenium(III) are formed, with higher values of the entropy changes (up to 84 J $mole^{-1}$ K^{-1}) compared with the OSC of tris(ethylenediamine)- and, probably, nitrosylpentammineruthenium(III) [137] ($\Delta S^0_1 \cong 54$–57 J $mole^{-1}$ K^{-1}), in contrast to the relationship observed for other metals. This is apparently due to the greater dehydration of the cationic complexes on the formation of the OSC of chloropentammineruthenium(III), compared with tris(ethylenediamine)ruthenium(III).

The stability of the OSC of tris(ethylenediamine)ruthenium(III) decreases[29] in the order of outer-sphere ligands: thiosulphate > sulphate > sulphite > selenite > sulphate ions, and that for chloropentammineruthenium(III) in the order: thiosulphate > sulphate > selenite > sulphite ions, but the decrease is small [the free energy changes for tris(ethylenediamine)ruthenium(III) and chloropentammineruthenium(III) in solutions with zero ionic strength are 0.5 kJ $mole^{-1}$ and 1.6 kJ $mole^{-1}$ respectively]. In aqueous solutions with zero ionic strength, the stability of the OSC of ruthenium(III) decreases in the following order of cationic complexes[31]:

$$[Ru(NH_3)_5(NO)]^{3+} > [Ru(en)_3]^{3+} > [Ru(NH_3)_5Cl]^{2+}.$$

The strong π-acceptor properties of the nitrosyl group and the possible resulting change in the actual state of ruthenium from Ru^{III} to Ru^{IV} [138] are responsible for the high stability of the OSC of $[Ru(NH_3)_5(NO)]^{3+}$ compared with those of $[Ru(en)_3]^{3+}$; the replacement of the nitrosyl group in the inner sphere of the cationic complex by chloride ion decreases the stability of the resulting OSC, since the charge on the cationic complex is lowered.

Unlike the OSC of the tris(ethylenediamine) compounds of cobalt(III), rhodium(III),[26,92,125] and chromium(III),[78] for the OSC of tris(ethylenediamine)ruthenium(III),[31] increased ionic strength of the solution leads to an increase in the positive values of the enthalpy changes and to a decrease in the contribution of the entropy component of the free energy.

VI. SOME GENERAL REGULAR FEATURES OF THE THERMODYNAMICS OF THE FORMATION OF OUTER-SPHERE COMPLEXES

Analysis of the data in Tables 4, 5, and 9–12, and the fairly accurate published data[106–109], show that entropy changes of $\Delta S_1^0 = 63 \pm 8$ J mole^{-1} K^{-1} and $\Delta S_2^0 = 29 \pm 8$ J mole^{-1} K^{-1} accompany the addition of the first and second doubly-charged anions to the great majority of hydrophilic coordinately-saturated inert and labile cationic complexes with charges from +1 to +4 in aqueous solutions with zero ionic strength at temperatures close to 298 K. The removal of one solvent molecule from the inner sphere of a cation into an aqueous solution leads to an entropy change of 30.54 J mole^{-1} K^{-1}.[139,140] This value is close to the entropy of fusion of ice[141] and to the entropies of water molecules coordinated, for example, to praseodymium(III) or ytterbium(III).[142] If it is assumed that the difference in the partial molar entropies of the associate and the ligand of the cationic complex is close to zero, it may be concluded that the addition of the first doubly-charged anions in the inner sphere is accompanied by the liberation of two water molecules.

The liberation of two water molecules on the addition, in the inner sphere, of the first doubly-charged anions to both hydrophilic and hydrophobic cationic complexes is indicated by data on the formation constants of OSC in aqueous-organic solutions (Tables 2 and 3). The entropy changes for the formation of OSC by hydrophobic cations (Table 7) do not indicate unambiguously the removal of two water molecules, since they are negative.

It has been suggested that sulphate ions are dehydrated when they add on to cations[106,107]. On the other hand, the difference in the entropy changes in the first and second stages of outer-sphere association provide a basis for assuming that water molecules are liberated as a consequence of dehydration of the cationic complex[26,98,124].

Increase in the ionic strength of the solution should decrease the magnitude of the entropy changes for the formation of OSC, if these changes are related to the dehydration of the anion–ligand, since the water hydrating this anion reaily combines with other ions. This is not observed in all systems, however[26,92,125]. At the same time, for hydrophobic cationic complexes it is necessary to assume that ions can associate by the combination of cavities or the entry of two ions into one cage created by the solvent[123]. In this process, the liberation of water molecules may take place from distant spheres of the hydrated cationic complex or from the anion–ligand.

The great majority of research workers consider that the formation of the first acido-OSC, like that of ordinary ion pairs, can be described[45,106,107] by the electrostatic theories of Bjerrum and Fuoss[143,144]. The processes of OSC formation should take place with a decrease in enthalpy and an increase in entropy[23], since according to these theories it is possible to write

$$\Delta H_1^0, \text{kJ mole}^{-1} = 0.891 \cdot b$$

$$\Delta S_1^0, \text{J mole}^{-1}\text{K}^{-1} = 58.16 \cdot \lg a^0 + 11.3 \cdot b - 49.8$$

where a^0 is the distance of closest approach of the associating ions, $b = z_C z_A e^2/\varepsilon k T a^0$, where z_C and z_A are the charges on the complex and the outer-sphere ligand, e the charge on the electron, ε the dielectric constant of the solvent, and k the Boltzmann constant.

Thus for charges of the associating ions equal to 1, 2, and 3, and $a^0 = 0.357$ nm, the enthalpy changes should be equal to[23] 1.7, 7.1, and 15.9 kJ mole^{-1}, and the entropy changes 5, 73, and 177 J mole^{-1} K^{-1} respectively. Increase in a^0 to 0.714 nm changes these values[23] to 0.8, 3.3, and 8.0 kJ mole^{-1}, and 11.3, 45.2, and 101.7 J mole^{-1} K^{-1}. The data in Tables 5, 10, and 11 show that the model based on the theories of Bjerrum and Fuoss effectively describes the changes in the thermodynamic functions for the formation of OSC by doubly-charged hydrophilic complexes with doubly-charged anions for $a^0 = 0.3$–0.5 nm. The associates of triply-charged hydrophilic cations with doubly-charged anions correspond only approximately to this model. The experimental data indicate, however, that the positive values of the enthalpy changes increase with decrease in the charge on the cationic complex (according to the theory, the positive values of the enthalpy should decrease[23]), and the positive values of the entropy change remain practically unchanged or increase slightly (according to the theory, the positive values of the entropy changes should decrease[23]). The changes in the thermodynamic functions for the formation of OSC by hydrophobic cations with doubly-charged anions (see Table 7) do not agree at all with the theories of Bjerrum and Fuoss[106,107] or with Ahrland's concept[106,107].

On the basis of the fact that the entropy changes for the formation of OSC by hydrophilic cationic complexes with doubly-charged anions are practically constant, and the regular decrease in the stability of the OSC with decrease in the charge of the complex and increase in the positive values of the enthalpy changes, some authors have predicted the values of the thermodynamic functions for the formation of OSC in systems which have not yet been studied[26,45]. For several systems, it has been found that the predicted values are close to those determined experimentally.

The formation of OSC by coordination compounds of cobalt(III), rhodium(III), chromium(III), and platinum(IV) is concentrated electrolyte solutions at 298 K is accompanied by free energy changes in the range ±(2–4) kJ mole^{-1}; the enthalpy and entropy changes lie in the range ±40 kJ mole^{-1} and ±(80–120) J mole^{-1} K^{-1}.[49,57,69–77,92–102] According to Ref. 26, there is a compensation effect between the values of the enthalpy and entropy changes under these conditions.

The lack of data on the thermodynamics of the OSC of inert coordination compounds of the transition metals at present makes a wider generalisation impossible (particularly for multiligand OSC). An increase in the volume of information and an increase in the accuracy and reliability of the experimental data are necessary.

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Electron Paramagnetic Resonance of Free Radicals in the Two-millimetre Wavelength Range

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Experimental data obtained in recent years on the electron paramagnetic resonance (EPR) of free radicals in the two-millimetre wavelength range are surveyed. It is shown that measurement of the spectra in this range makes it possible to increase greatly the amount of information derivable by the EPR method and its absolute sensitivity. The results of measurements of the magnetic resonance parameters of nitroxy-radicals, nitroxy-biradicals, and peroxy-radicals as well as data on the molecular mobilities of the above radicals in various matrices are presented.
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I. INTRODUCTION

The vigorous development of experimental methods whereby the amount of information derivable by the EPR method is increased and which open up completely new fields in which the method can be applied has taken place at the present time. The new fields include magnetic resonance laser spectroscopy in the submillimetre and near infrared ranges, used to investigate free radicals in the gas phase[1-3], the spin echo electron spectroscopy[4,5], used mainly to investigate the paramagnetic centres in solids, various combined methods employing the spin polarisation effects in which the EPR signal is recorded optically or from the change in the yield of the chemical reaction[6-10], saturation transfer spectroscopy[11], EPR in inhomogeneous fields (EPR tomography)[12], and a number of other new methods.

However, the majority of the methods indicated are applicable only to the solution of specific problems and to the investigation of specific objects. We shall consider the development of a new universal EPR technique associated with a sharp increase of the frequency of the measurements. For species with spin paramagnetism, an increase of the frequency of the measurements is associated simultaneously with the necessity to increase the magnetic field strength. Therefore, in contrast to experiments in the gas phase where the rotational or vibrational Zeeman transitions are used, in the case of spin-only resonance progress has been made virtually only in the two-millimetre wavelength range. However, in this range studies on the EPR of free radicals, biradicals, and certain paramagnetic complexes carried out in recent years at the Institute of Chemical Physics of the USSR Academy of Sciences have already yielded what we believe to be extremely interesting and very promising results. The state of this field is considered in the present review.

II. EPR IN THE MILLIMETRE RANGE: GENERAL PRINCIPLES AND POSSIBILITIES OF MEASUREMENT

The switch to stronger magnetic fields and the corresponding increase of the frequency of the measurements should in principle improve the fundamental characteristics of the magnetic resonance spectrometers: sensitivity and resolving power. Thus the sensitivity of EPR spectrometers is proportional to ω^{α}, where α assumes values ranging from 1/2 to 9/2 depending on the conditions of the measurement. It follows from the condition for magnetic resonance $\omega = \gamma H$ that, for centres of different types differing in the gyromagnetic ratio γ, the resonance fields at a fixed frequency of the measurement ω differ more the higher this frequency.

It can be shown on the basis of the most general physical considerations that the optimum, from the standpoint of the amount of information which can be derived, frequency of the observation of the magnetic resonance corresponds to kT/h in order of magnitude and occurs in the range $10^{12}-10^{13}$ Hz at the usual temperatures, i.e. constitutes the "physically optimal" submillimetre wavelength range.

Practice gained in NMR research has shown that a switch to the measurement of magnetic resonance in strong fields with a corresponding increase of the resonance frequency makes it possible to realise the possibilities underlying this procedure for the improvement of the sensitivity and spectral resolution. Whereas 20 years ago the 10-40 MHz wavelength range was usually employed, at the present time NMR is recorded in the wavelength range 300-400 MHz. On the other hand, in EPR the three-centimetre or X-range has been dominant during three decades. The explanation is that the experimental basis of the EPR spectroscopy, which was for a number of reasons developed from the very beginning in the 3-cm range, proved to be extremely successful and satisfied for many years the requirements of experimenters as regards sensitivity and resolution and also made it possible to combine readily EPR with various sources of the generation of paramagnetic species and with other research techniques. Another cause is probably that, in contrast to NMR, the usefulness of using high transitions in EPR is not quite so evident. Indeed, the basis of the increase of the spectral resolution with increasing magnetic field strength in NMR is the great variety and specificity of the chemical shifts for nuclei of different functional groups. The analogue of the chemical shift in EPR, which determines the displacement of the resonance lines with increasing field strength, is the g-factor.

For free radicals, which are the main objects of EPR studies in chemical physics, biology, and medicine, the values of g are near those of the g-factor of the free electron ($g_e = 2.0023$) and in most cases are not characteristic as the chemical shift in NMR. Bearing

in mind that experimenters have a large source of information in the field of EPR, namely the hyperfine and fine structures, one can imagine that interest in EPR studies in strong fields was insufficient to overcome the technical difficulties arising in this connection, which significantly held back the development of millimetre EPR spectroscopy. In particular, in the millimetre range not all the elements of the microwave technique are equivalent to those employed at the 3-cm range. Furthermore, here it is not always possible to use the best constructional solutions found for 3-cm EPR spectrometers. It was therefore expected that the sensitivity of a spectrometer of the millimetre range would not exceed or would even be inferior to the sensitivity of spectrometers for the 3-cm range.

Thus, general considerations alone are insufficient to provide an answer to the question of the likely usefulness of the development of high-frequency EPR; a special and broadly based series of experiments is necessary.

Fairly numerous studies in wavelength ranges below 3 cm are now available : in the K-range (12 mm) and the Q-range (8mm). An improvement of the absolute sensitivity of 2×10^{10} spins G^{-1} in the 3-cm range to 5×10^{9} spins G^{-1} in the Q-range was indeed achieved. However, in view of the increase of the working volume of the specimen, due to the decrease of the size of the measuring cell, the concentration sensitivity of such spectrometers was not improved.

We shall now turn to the problem of spectral resolution. At the present time one of the significant difficulties in the interpretation of the spectra consists in the identity of the g-factors for different radicals, which leads to the superposition of their spectra. This hinders greatly the interpretation of the spectra and the derivation of information from them; in particular, it precludes the use of the values of g as a source of information about the structure of the radicals. An analogous situation arises also in the absence of superimposed signals in the analysis of weakly anisotropic spectra in frozen solutions and powders[13].

The values of g for typical organic radicals differ from one another by $(1-10) \times 10^{-4}$. In the study of the signals in the three-centimetre range usually employed this leads to a line shift with respect to the field of 1–10 G and the overall extent of the spectra (taking into account the hyperfine structure) is 10–100 G. Comparison of the above values shows that, for an effective resolution of the spectral components of different free radicals, it is necessary to increase the working frequency by more than an order of magnitude compared with the centimetre EPR range, i.e. it is necessary to switch to the millimetre range for the measurement of EPR. According to estimates, a switch to the 12- and 8-mm ranges is in most cases insufficient for the effective resolution of the spectral lines.

In measurements at a wavelength $\lambda < 3$ mm the resolution should be sufficient in most cases, provided that the width of the individual line at least does not increase in this frequency range. Theoretical models predict a wide variety of line width–frequency relations, involving both a sharp increase and a sharp decrease, so that only systematic measurements can solve the problem of the likely usefulness of the millimetre range in high-resolution EPR.

The creation of spectrometers for the 1–3 mm range, suitable for the solution of physicochemical problems, requires the elucidation of a set of questions: (1) the question of sources, transmitting elements, and detectors for the millimetre and submillimetre radiations; (2) the question of the magnetic system of the spectrometer ensuring sufficiently intense fields, which must be varied and scanned over a wide range with retention of the high stability and homogeneity of the field; (3) the question of temperature control and the replacement in the course of the experiment of specimens of different types, including liquid and vitreous specimens.

Sources of the most traditional type in EPR spectroscopy consist of klystron oscillators. A series of their instruments and devices using wavelength ranges down to 2 mm have now been made based on the klystron. Thus the second harmonic of the klystron oscillator for the 4-mm range is used in the specrometer described in a monograph[14]. A specially developed klystron for the 2-millimetre range has been employed[15]. Backward-ware oscillators (carcinotrons[16]) have found extensive applications in spectrometers for the millimetre range; with their aid, it is possible to proceed to still shorter wavelengths[17].

With the aid of laser sources, it is possible to move into the infrared range and beyond. However, one must not forget that in the spectroscopy of free radicals an increase of the frequency of the spectrometer requires a proportional increase in the polarising magnetic field. Thus a field of ~1 MG is required for $\lambda = 0.1$ mm. Field strengths of 1 MG in an EPR spectrometer have been achieved[18] under pulsed conditions within a multisection solenoid of special design and pulsing lasers with the working wavelengths $\lambda = 337$ μm (based on HCN vapour) and $\lambda = 119$ μm (based on H_2O vapour) have been used as sources of radiation. Unfortunately, a spectrometer constructed on this principle cannot apparently be used for extensive studies of free radicals in view of its low concentration sensitivity due both to the obligatory broad recording band (for an amplitude of 1 MG of a pulsing field with a duration of 200 μs, the time taken to traverse a signal with a width of 10 G is 2 ns) and to the large on-off time ratio of the pulses. Furthermore, it is impossible to avoid the occurrence of large distortions in the shape of the spectrum which are difficult to analyse. Nevertheless, in cases where these factors do not play a significant role, such a spectrometer does indeed make it possible to obtain interesting information, which is not accessible by other methods[19].

The most promising magnetic systems are based on a superconducting solenoid. Superconducting 50–100 kG systems, in which the magnetic fields are generated in fairly large volumes, are nowadays commercially available and are fairly widely used in NMR. It is noteworthy that, since fairly large changes in the magnetic field strength are necessary in the course of the experiment during EPR measurements, the magnet of the EPR spectrometer must operate under the given power supply conditions and the cryomagnetic systems of NMR spectrometers operating under frozen field conditions are unsuitable for direct use in an EPR spectrometer. Appropriate modification of the magnetic system and its power supply do not apparently present fundamental difficulties.

The availability of the principal elements of EPR microwave spectrometers—magnetic systems, oscillators, and detectors (high-temperature crystalline and low-temperature n-InSB detectors)—made it possible to create a whole series of specialised EPR devices for the millimetre range[16,20–24]. It is noteworthy that the apparatus employed in the above studies had a limited scope with respect to two parameters which are of central importance in physicochemical research, namely sensitivity and the possibility of extensive variation of the temperature of the measurement.

The greatest possibilities for an increase of sensitivity involve the optimisation of the measuring cell of the spectrometer. In measurements using the simplest "through" circuits without a resonator, the sensitivity is minimal and amounts to 10^{13}–10^{14} spins G^{-1}.[24] The situation improves when extra large resonators[15] or Fabry–Perrault resonator interferometers[25] are used. However, these resonators

cannot be regarded as the best: in order to avoid unduly large losses of energy, it is necessary to employ specimens of special shape (which to not distort the distribution of the microwave field) and small size, i.e. to ensure low filling coefficients. We believe that the best solution involves the employment of low-mode volume resonators analogous to those employed in the X-range. Thus an absolute sensitivity of 4×10^7 spins G^{-1} and a concentration sensitivity of 2×10^{11} spins cm^{-3} G^{-1} have been obtained for a resonator of type H_{011} in the 2-mm range[26].

In spectrometers with a superconducting solenoid the specimen is placed within the solenoid and hence within a helium cryostat. The conditions in the EPR measurements are then necessarily limited to temperatures in the vicinity of 4 K; access to this specimen for its replacement and various manipulations is also hindered. In order to ensure the possibility of regulating the temperature of the specimen within a wide range, it is essential that the cryostat be provided with a thermally insulated working chamber for the measuring cell (as, for example, in the study of Galkin et al. [15]).

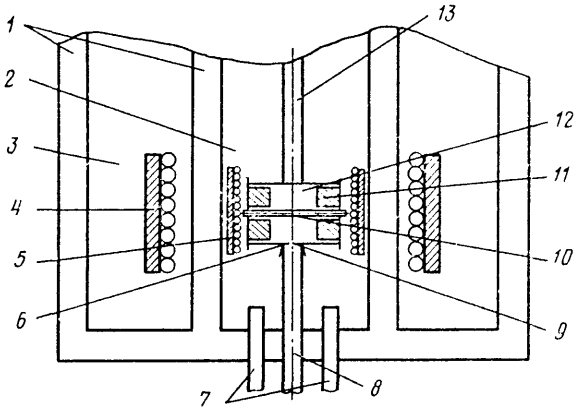


Figure 1. Schematic illustration of the positioning of the resonator in the working chamber of the cryostat of the EPR spectrometer for the two-millimetre range: *1*) thermally insulated vacuum jackets; *2*) working chamber; *3*) liquid helium; *4*) superconducting solenoid; *5*) magnetic modulation coils; *6*) disconnectable junction between the resonator and the UHF supply waveguide; *7*) inlet and outlet for the heat exchanger in the thermal stabilisation system; *8*) UHF supply waveguide; *9*) aperture for the adjustable linkage; *10*) bulb for the specimen 0.7 mm in diameter; *11*) adjustable piston for the adjustment of the volume of the resonator; *12*) cylindrical H_{011} resonator; *13*) fixing rod for the resonator and the regulating mechanims[26].

The above discussion shows that an EPR spectrometer for the 2-mm range with a polarising field up to 70 kG, with provision for the regulation of the temperature of the measurement within a wide range and with a sensitivity sufficient for the investigation of the majority of objects traditional in EPR spectroscopy, is at present entirely realistic. The concentration sensitivity attained in the 2-mm range is comparable to the sensitivity of standard spectrometers for the 3-cm range and the absolute sensitivity is greatly superior to the latter. This created conditions for the formulation of experiments designed to elucidate the prospects for the employment of EPR in the millimetre range in the study of free radicals.

A cryostat with a temperature controlled working chamber, in which was placed a type H_{011} resonator with a special tuning system and the junctions between the resonator and the waveguide, ensuring a rapid replacement of the specimens in the course of measurements, was incorporated in the EPR spectrometer for the two-millimetre range[15] which is used nowadays in the Institute of Chemical Physics of the USSR Academy of Sciences (Fig.1). So far as we are aware, this is at present the only experimental apparatus permitting the measurement of electron spin resonance spectra in the two-millimetre wavelength range for liquid, vitrified, and powdered specimens over a wide temperature range (100–350 K) and with a fairly high concentration sensitivity (2×10^{11} spins G^{-1} cm^{-2}). As already mentioned, the absolute sensitivity is 4×10^7 spins G^{-1} at room temperature and is maximum for EPR (a higher sensitivity can be achieved only in "on-equilibrium" experiments with optical or "chemical" recording of the signal[7,8] but such experiments are possible only for special objects). Liquid, frozen, and friable specimens were placed in a capillary ~0.7 mm in diameter (0.2 mm) for aqueous solutions), which was located on the resonator axis: solid single crystal specimens can be attached on the bottom of the resonator or on a special rod. The majority of the results described above were obtained on this apparatus. The system illustrated in Fig.1 is unsuitable for the study of specimens in the form of suspensions, native tissues, etc., which are difficult to insert into a thin capillary. Resonators of the Fabry–Perrault type can probably be usefully employed for specimens of this kind.

III. DETERMINATION OF THE MAGNETIC RESONANCE PARAMETERS AND THE STRUCTURE OF FREE RADICALS AND BIRADICALS

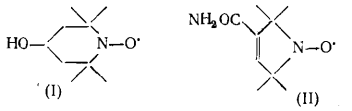
The g- factor of the paramagnetic centre (or the set of g-tensors) is one of the fundamental magnetic-resonance parameters[27]. The first systematic study undertaken in order to employ the g-factors to obtain physicochemical information about free radicals is apparently that of Stone[28]. He developed a general theory relating to g-factor to the molecular and electronic structure of the radical, devised a semi-empirical method for the calculation of g-factors, and compared the calculated and experimental data. Subsequently a whole series of similar studies were carried out in which the influence of solvents on the g-factor was considered apart from structural aspects and various modifications of Stone's theory were developed. Aromatic radicals[29], semiquinones[30], phenoxy-radicals[31], nitrofuran radical-anions[32], nitroxy-radicals[33], peroxy-radicals[34], and other radicals were investigated in succession. The possibility of the experimental observation and fairly accurate measurement of the changes in the g-factors within a "homologous" series of compounds or solvents was of decisive importance in these investigations.

Several studies devoted the the analysis of the accuracy of the experimental determination of the g-factor have been described[35,36]. The procedure involving the relative measurement of the g-factor on the basis of the shift of the given line relative to the reference signal is most widely used and is most convenient. In measurements of this type there is no need for the simultaneous accurate determination of the absolute frequency and field strength and it is sufficient to measure the resonance field of the reference line and the distance from the latter to the measured line with a much lower accuracy. The precision of such measurements is,

however, lower the greater the width of the individual components of the spectrum. Thus only solutions of radicals having EPR spectra with fairly narrow lines, whose width does not exceed 0.1–0.3 G, are susceptible to studies in the 3-cm range. The switch to the millimetre EPR range makes it possible, in principle, to increase greatly the accuracy of the measurements of the components of the g-tensor and thus to extend greatly the class of objects susceptible to investigation.

However, one should bear in mind that an improvement of resolution would be observed when addtional line broadening does not occur following an increase of the resonance frequency. As already mentioned, only experiment can lead to the discovery of systems in which a real improvement of the resolution of the spectra in measurements in the millimetre EPR range is possible.

Measurements in the millimetre range of the EPR spectra of free radicals with $g = 2$ in solution at room temperature were achieved for the first time in 1976.[37] Fig. 2 presents the spectra of a solution (10^{-3}M) of a mixture of stable radicals (I) and (II) in dioxan[37]:



Spectrum a, obtained on a standard spectrometer for the three-centrimetre range, demonstrates a virtually complete supersposition of the components of the individual spectra. Fig. 2b illustrates the complete resolution of the components of the individual spectra in measurements on a spectrometer for the two-millimetre range. The difference between the g-factors for radicals (I) and (II) is $\Delta g = 2.40 \times 10^{-4}$. The accuracy of the relative measurements is to within a factor reaching 10^{-5}, which makes it possible to employ the g-factor as an effective characteristic of individual paramagnetic compounds. Fig. 2b also shows that the width of the individual lines of the spectrum hardly changes on passing from the three-centimetre to the millimetre range.

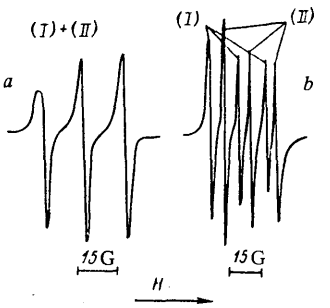


Figure 2. EPR spectra of solutions of a mixture of radicals (I) and (II) (1:1), 10^{-3}M) in dioxane. Measurements at 300 K on spectrometers for the 3-cm (a) and 2-mm (b) ranges[37].

In certain systems, usually in solids, such a transition leads to an additional broadening of the lines, but an improvement of the resolution is nevertheless still attained. An example of this type is provided by the peroxy-radicals $RO_2^{\cdot}$ investigated by Grinberg et al.[38], The simplest radicals of this series, namely $HO_2^{\cdot}$, were obtained in the photolysis of a 30% frozen H_2O_2/H_2O solution at 77 K. In contrast to the 3-cm range, in the 2-mm range the resonance lines corresponding to the radicals in which the principal axes of the g-tensor are directed along the external magnetic field canonical components) are fully resolved (Fig. 3a), which made it possible to determine the main values of the g-tensor ($g_1 = 2.00382$, $g_2 = 2.00821$, and $g_3 = 2.03362$). After heating the specimen to 140 K, some of the $HO_2^{\cdot}$ radicals recombined, which led to a narrowing and shift of the lines: $\delta g_1 = -1.05 \times 10^{-3}$ and $\delta g_2 = 1.33 \times 10^{-3}$. These changes in the EPR spectrum indicate, on the one hand, the structural inhomogeneity of the specimen as a possible cause of the additional line broadening in the two-millimetre spectra; on the other hand, they indicate a correlation between the stability of the radicals and their environment. Differences between the magnetic parameters of the middle (R_mO_2) and terminal (R_tO_2) peroxy-radicals in polytetrafluoroethylene have also been observed[38] (Fig. 3b). The principal values of the g-tensor were obtained: $g_1^m = 2.00232$; $g_2^m = 2.00743$; $g_3^m = 2.03813$; $g_1^t = 2.00278$; $g_2^t = 2.00770$; $g_3^t = 2.03963$.

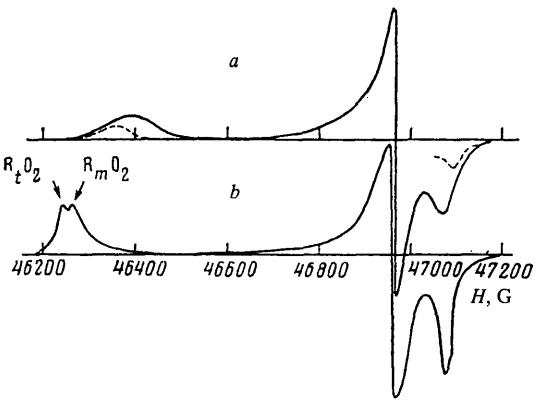


Figure 3. EPR spectra of peroxy-radicals in the 2-mm range: a) in H_2O_2/H_2O at 77 K; dashed line—after annealing at temperatures up to 140 K; b) in polytetrafluoroethylene[38].

Fig. 4a presents yet another example which demonstrates the complete separation of the spectra of the peroxy-, alkyl, and allyl radicals in polytetrafluoroethylene as a result of the effective resolution by the spectrometer in the two-millimetre range. The spectrum for the same specimen recorded in the 3-cm range, illustrated in Fig. 4b, is an unresolved blend of overlapping spectra unsuitable for analysis. The examples presented show clearly that the switch to the millimetre EPR range for free radicals in condensed media does indeed entail an improvement of the resolution with respect to the g-factor, which permits the separate recording of the group of lines of different radicals. On the other hand, the advantages of high-resolution spectroscopy can be used for the analysis of complex spectra of radicals of the same type when canonical groups of lines are resolved with increase of the resonance field strength. Figs. 5 and 6 present as examples the spectral solutions of the familiar compound $VOSO_4$ in H_2O and of the stable diphenylpicrylhydrazyl radical (DPPH) in toluene. Fig. 5 shows how appreciable is the simplification of the overall form of the spectrum of the vanadyl group in

the two-millimtre range compared with the spectrum in the three-centimetre range as a result of the separation of the components with perpendicular and parallel orientations to give isolated groups. On the other hand, the DPPH spectrum (Fig.6) shows the appearance of additional components but their positions make it possible to extract new information, inaccessible in measurements in the 3-cm range, about the components of the A and g tensors of the radical in a frozen toluene solution: $A = 20.9$ G and $g_{\parallel} = 2.00254$. It is noteworthy that a qualitative demonstration of the possibility of the resolution of the anisotropic doublet in the spectrum of DPPH powder was achieved as early as 1964.[16]

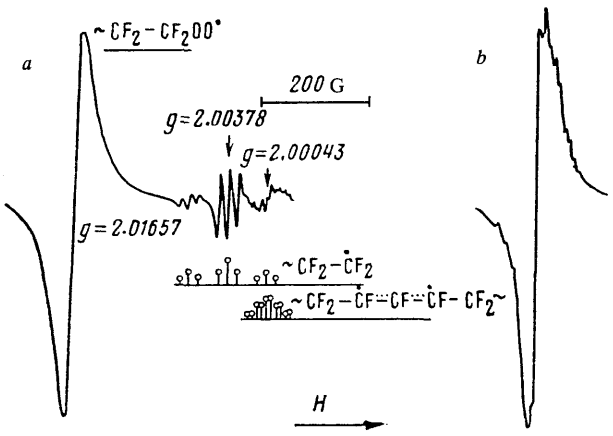


Figure 4. *a*) Separation of the EPR signals of the allyl, alkyl, and peroxy-radicals in polytetrafluoroethylene in the 2-mm range; *b*) spectrum of the same specimen in the 3-mm range[38].

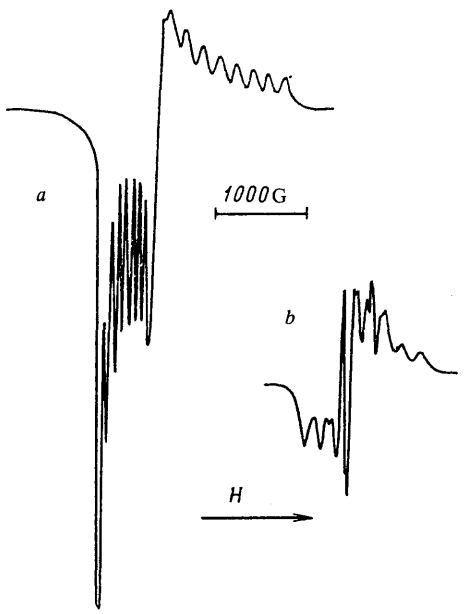


Figure 5. EPR spectra of VO^{2+} ions in sulphate glass in the 2-mm (*a*) and 3-cm (*b*) ranges[26].

The possibility of determining the principal values of the g- and A-tensors, which appears in the two-millimetre range, is particularly valuable in the case of nitroxy-radicals, which are widely used in chemical, biological, and medical research as spin probes and labels[39]. In order to obtain such information in the 3-cm range, the EPR spectra of single crystals, containing radicals as regular inclusions, were investigated. The preparation of such single crystals is difficult. Furthermore, the application of the method of spin labels and probes requires the introduction of radicals into different and as a rule non-single crystal matrices. Since the medium can influence the magnetic parameters[40], the employment of data obtained for single crystals is not always correct and inaccurate calculations of these data must be regarded solely as the zeroth approximation for undetermined variable parameters[39]. The magnetic resonance parameters measured directly in real polyoriented objects are therefore particularly valuable.

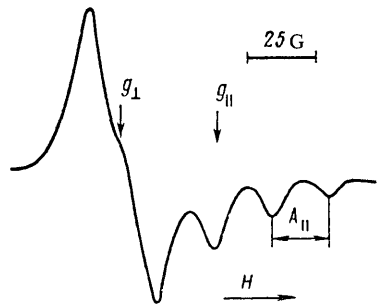


Figure 6. EPR spectrum of a frozen solution of DPPH in toluene in the 2-mm range[26].

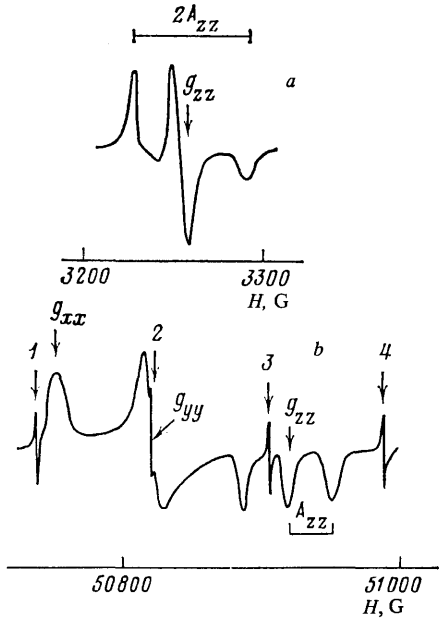
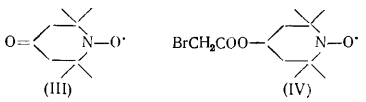


Figure 7. EPR spectra of a radical (III) solution in polystyrene at 77 K in the 3-cm (*a*) and 2-mm (*b*) ranges. The arrows indicate the components of the 1–4 spectrum of the Mn^{2+} lateral standard in MgO.

Fig.7 presents the spectra of a solid solution (10^{-3}M) of the stable radical (III) in polystyrene at 77 K.[37] Components corresponding to the three principal values of the anisotropic g-factor are distinctly seen in the spectrum obtained in the 2-mm range. One of the values of the anisotropic A-tensor can also be readily measured. Determination of the remaining principle values of the A-tensors (A_{xx} and A_{yy}) from the spectra of nitroxy-radicals of the type illustrated in Fig.7 is evidently difficult (z represents the direction at right angles to the plane of the radical fragment and x the direction along the N–O bond).



(III) (IV)

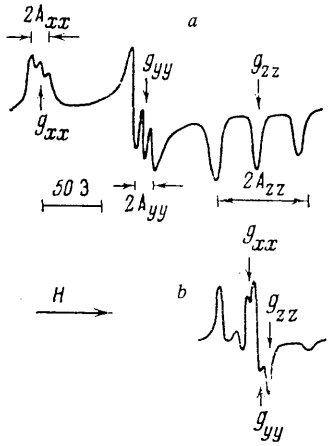
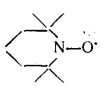


Figure 8. EPR spectra of a solution of deuterated radical (IV) in toluene at 140 K: *a*) 2-mm range; *b*) 3-cm range.

In order to improve the resolution of the UHF lines in the 2-mm EPR spectra, the familiar procedure of isotope substitution of H by D or of ^{14}N or ^{15}N has been used[41]. Fig.8*a* illustrates the spectrum of radical (IV) and the characteristic points from which the complete set of magnetic resonance parameters were determined directly. For comparison, Fig.8*b* presents the spectrum of the same radical in the three-centimetre range. It is noteworthy that for deuterium-substituted radicals there is a possibility, in principle, of determining the parameters also from the spectra in the 3-cm range[49]. However, this entails necessarily a complex analysis involving a theoretical calculation of the spectrum, which lowers the accuracy of the determination of the parameters and leads to a sharp increase of the time consumed. All the magnetic-resonance parameters of radical (V) with the ^{15}N isotope can be determined directly from the spectrum in Fig.9, as for the spectrum in Fig.8*a*.



(V)

The magnetic parameters of nitroxy-radicals of different types (about 70 individual structures) have been determined[43] from the EPR spectra in the 2-mm range. The principal values of the g-tensor of the nitroxy-radicals determined in the above study are presented in Fig.10 in terms of plots of g_{xx} against g_{yy} and g_{zz}. The figure shows that g_{xx} is most sensitive to the structure of the radical. It is noteworthy that the points corresponding to different radicals in the "space of g-factors" do not coincide in most cases, which permits the conclusion that the EPR resolution attained in the 2-mm range makes the g-tensor of nitroxy-radicals a characteristic parameter which extends the availabel range of analytical procedures. Analysis of Fig.10 shows that the values of g for nitroxy-radicals with identical structures of the radical ring are grouped in a definite region corresponding mainly to radicals of the given series. The values of g_{xx} for nitroxy-radicals of the piperidine series are in the range from 2.00975 to 2.01005, those for radicals of the 4-piperidine series are between 2.00955 and 2.00970, those for radicals of the 3-imidazoline series with the nitrone group are between 2.00917 and 2.00930, and those for radicals of the series without the nitrone group are in the range from 2.00905 to 2.00915, i.e. they decrease in the series of radical structures enumerated.

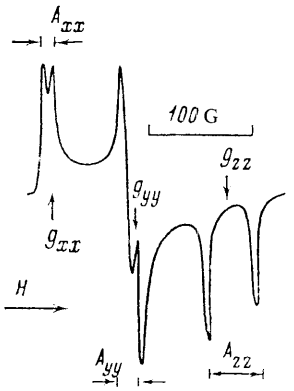


Figure 9. EPR spectrum of a solutlion of radical (V) with nitrogen substituted by ^{15}N in toluene at 140 K in the 2-mm range.

This behaviour, established in relation to a large number of radicals, is useful both in the assignment of the radicals to a particular class (i.e. in identification on the basis of EPR spectra) and in estimating the magnetic parameters of the radical on the basis of the type of its structure. These data are particularly important for the theoretical analysis of the structure of the radicals and its influence on the spectroscopic parameters. Thus in the series enumerated, there is a successive intensification of the interactions of π orbitals localised in the peripheral part of the radical with the π^* orbital of the N–O bond (the interatomic distance diminishes and the overlap of the orbitals improves), which alters the energy of the singly populated π^* orbital:

$$\delta E_{\pi^*} \simeq \Sigma \frac{V^2_{\pi^*\alpha}}{\Delta E_{\pi^*\alpha}} \qquad (1)$$

where α is the index of the peripheral orbital, $V^2_{\pi^*\alpha}$ the square of the matrix element approximately proportional to the overlap integral of the π^* and α orbitals, and $\Delta E_{\pi^*\alpha}$ the

difference between the energies of these orbitals. Overlap with the bonding peripheral π orbitals is more effective than with the antibonding orbitals, because in the latter there is partial compensation of the contributions by individual atomic orbitals. Terms with positive ΔE therefore predominate in the sum defined by Eqn.(1), which leads to an overall increase of the level of the singly populated π^* orbital of the NO group. The approximation[44]

$$\Delta g_{xx} = \lambda \rho_O^{\pi} / \Delta E_{n\pi^*}$$

is used for Δgxx. Here λ is the spin-orbital coupling constant for the oxygen atom, ρ_O^{π} the spin density at the oxygen atom, and $\Delta E_{n\pi^*}$ the energy of the $n-\pi^*$ transition.

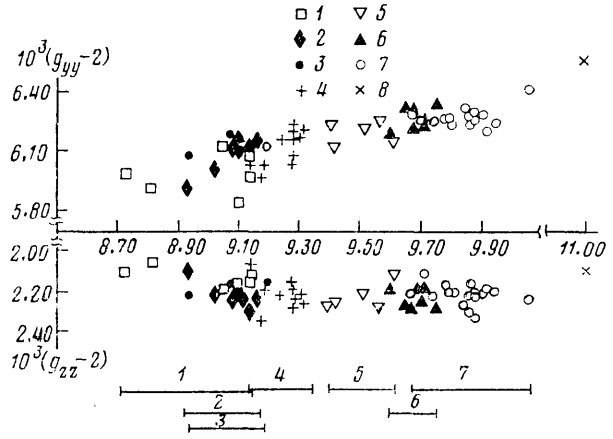


Figure 10. Principal values of the g-tensors for nitroxy-radicals having different structures; radicals derived from: *1*) imidazolidines; *2*) imidazolines; *3*) pyrrolidines; *4*) imidazolines with the N → O group; *5*) imidazolidines with phenyl substituents in the 4,4′-positions; *6*) 4-piperidines; *7*) piperidines; *8*) nitronylnitroxy-radical. The ranges incorporating the values of g_{xx} for radicals with the same ring structure are indicated below.

The positive shift δE_{π}^* leads to a decrease of gxx, which agrees with the relation discovered. Apart from the "direct" influence of peripheral orbitals described above, there are also other factors acting on gxx. It has been noted[43] that an increase of gxx is accompanied by an increase of the N-O bond length, a decrease of the angle between the N-O bond and the -C-N-C- plane, and the decrease of the CNC angle in the radical fragment. The examples presented show that high-resolution EPR (millimetre range) makes it possible to increase the accuracy of the measurement of the g-tensor components and to observe experimentally the fine changes in these quantities under the influence of various factors. The measured principal values of the A- and g- tensors can apparently be used to identify the radicals, in the study of the interaction of the radicals with the molecules of the medium, and in comparing spectroscopic data with the results of quantum-chemical calculations for radicals of different structures.

In certain cases it is possible to obtain from spectra in the two-millimetre range information about the structure of the centres investigated. The spectrum (Fig.11) of the middle peroxy-radical in polytetrafluoroethylene (PTFE), characterised by an axially-symmetrical g-tensor owing to the movement of the radical fragment around the polymer axis, has been recorded[44] at 300 K.

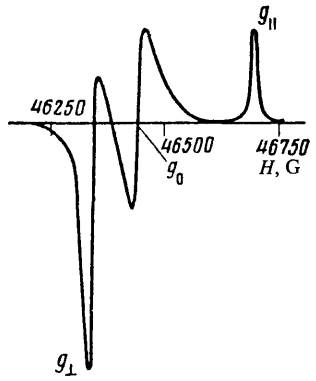


Figure 11. Spectrum of peroxy-radicals in polytetrafluoroethylene at 300 K; $g_{\parallel}$ and $g_{\perp}$ are components of the g-factor of the middle radical R_mO_2; g_0 is the component of the g-factor of the residual terminal R_tO_2 radical.

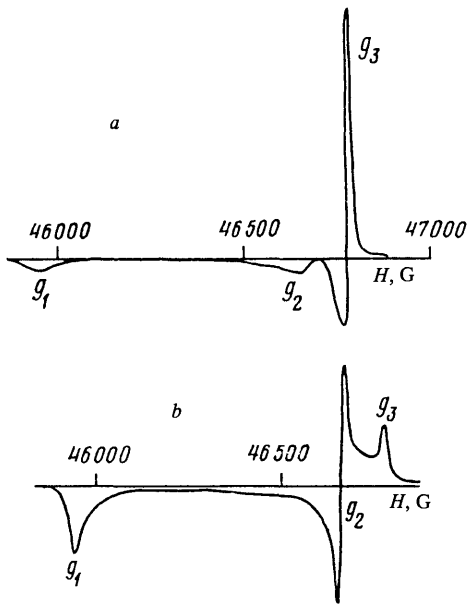


Figure 12. EPR spectrum at 100 K in the 2-mm range of the middle radical in polytetrafluoroethylene specimens oriented by stretching: *a*) extension axis parallel to the field; *b*) axis perpendicular to the field[44].

For radicals the axis of rotation of which is parallel to the external magnetic field, the presence or absence of rotation is in no way manifested in the EPR spectra. In the absence of rotation, the spectrum of these species are characterised by its g-factor

$$g = (g_1^2 l_1^2 + g_2^2 l_2^2 + g_3^2 l_3^2)^{1/2}, \qquad (2)$$

where l_i are the directional cosines of the axis of rotation relative to the principal axes of the g-tensor. For rapid rotation, the spectrum of these species in semioriented specimens corresponds to the components with $g = g_{\parallel}$. The above equation together with the relation

$$l_1^2 + l_2^2 + l_3^2 = 1 \qquad (3)$$

defines the curve on the surface of a single sphere—the geometrical locus of the possible positions of the end of the vector of the directional axis of rotation. Additional data about the position of the axis of rotation have been obtained from the spectra of partially oriented polytetrafluoroethylene specimens. Fig.12 shows that, when the axis of extension of the specimen is oriented along the magnetic field, the intensity of the g_2 component falls sharply. Consequently the molecular axis corresponding to this component is located near the plane perpendicular to the axis of extension. Having assumed that the axis of rotation coincides with the longitudinal axis of the molecule, which is oriented along the axis of extension during the stretching process, one can find that $l_2 \cong 0$. This estimate and Eqns.(2) and (3) made it possible to establish, after substituting the values of g_i, that the polymer axis in the XY plane makes an angle $\theta = 72°$ with the direction of the O–O bond. The location of the CO_2 fragment in the polytetrafluoroethylene molecule and the orientation of the principal axis of the g-tensor relative to the molecular axis are shown in Fig.13.

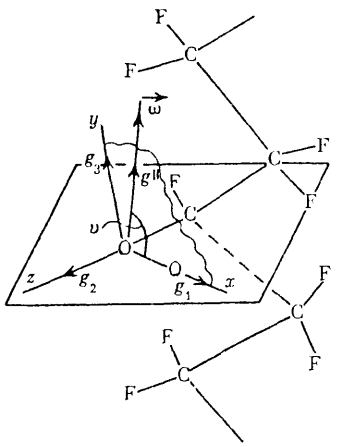


Figure 13. Disposition of the CO_2 fragment and of the principal axes of the g-tensor for the middle peroxy-radical relative to the polytetrafluoroethylene molecule[44].

The application of two-millimetre EPR holds out promise for extensive possibilities in the study of the structures of biradicals. Fig.14 illustrates the EPR spectra of a toluene solution of the *trans*-bis(2,2,5,5-tetramethyl-3-oxo-3-imidazolin-1-oxy-4-yl)ethylene biradical in the 3-cm and 2-mm ranges. Preliminary inspection showed already that the spectrum in the two-millimetre range is simpler and more convenient for analysis. The components in the spectrum in Fig.14 can be assigned by comparison with the spectrum of the monoradical (Fig.7). The spectrum of the biradical has a greater multiplicity of lines in the hyperfine structure (HFS) compared with the spectrum of the monoradical: the electrons of the biradical interact with the magnetic nuclei of both fragments. Furthermore, a doublet dipole–dipole line splitting appears. The spectrum illustrated in Fig.14*a* results precisely from the splitting of the canonical components in the spectrum of the monoradical (Fig.7) into dipole doublets when account is taken of the increase of the HFS multiplicity manifested in the z components.

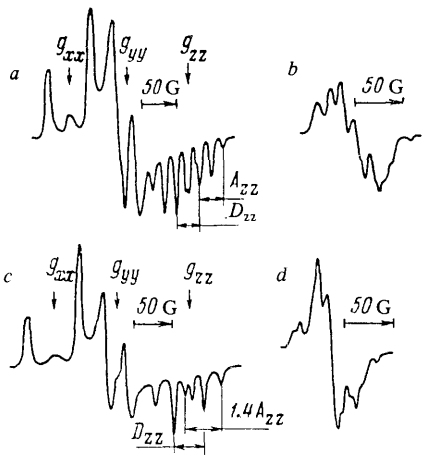


Figure 14. EPR spectra of nitroxy-biradicals (structure shown in Fig.15) in a 10^{-3} M solution in toluene at 140 K: *a*) and *b*) with ^{14}N atoms; *c*) and *d*) with ^{15}N atoms; *a*) and *c*) in the 2-mm range; *b*) and *d*) in the 3-cm range[45].

The positions of the components in the spectrum of the biradical are determined by the set of parameters characterising its structure and magnetic interactions, in particular the principal values of the fine structure D-tensor and the relative orientations of the axes of the g- and D-tensors. It has been established[45] that the axes of the g-tensors of both nitroxy-fragments of the biradical have the same directions and that the symmetry axis of the D-tensor is in the xy plane of the g-tensor and makes an angle of 14° with the x axis of the g-tensor.

The geometrical structure of the biradical was established on the basis of the data obtained: the molecule has a planar structure and the *cis*, *trans*, *cis*-conformation relative to the C(5)–C(6), C(6)–C(6′), and C(6′)–C(5′) axes (Fig.15). Quantitative estimates of the delocalisation of the spin density from the NO radical fragment to the π-system of the C(3)–C(4)...C(4′)–C(3′) biradical have shown that the spin densities in the atomic orbitals of these nuclei are ~1%.

The examples considered demonstrate that, in the measurement of the spectra of free radicals in the 2-mm range in condensed media, an additional broadening of the individual lines is not as a rule observed. An increase of the resonance frequency entails a real increase of the resolution of the EPR spectra of free radicals which makes it possible to record separately the spectra of different radicals in the mixture, increases the accuracy of the measurement of the g-factors, and simplifies or simply makes possible the analysis of the spectra of the paramagnetic centres. From our point of view, the results presented justify the treatment of the spectroscopy in the millimetre range as high-resolution EPR spectroscopy with respect to the g-factor, which can yield valuable

physicochemical information about the structure of the paramagnetic species and their interaction with the medium.

IV. THE STUDY OF MOLECULAR MOVEMENTS

Studies of the molecular mobility in condensed media occupy a notable place in modern researches by EPR. Such investigations are based on the sensitivity of the form of the EPR spectra to the relaxation processes caused by the movements of the paramagnetic centres and their environment. The method of spin labels and probes, developed largely for the investigation of molecular mobility in biological objects[39] and polymeric matrices[46], has become particularly widespread. However, one already has to reckon with the limitations to this method associated, in particular, with the inadequate resolution in the spectra of typical labels (stable nitroxy-radicals are usually employed as labels and probes[39]). In this situation it is natural to use procedures which improve the spectral resolution, the most effective of which involves the measurement of the EPR spectra in strong fields.

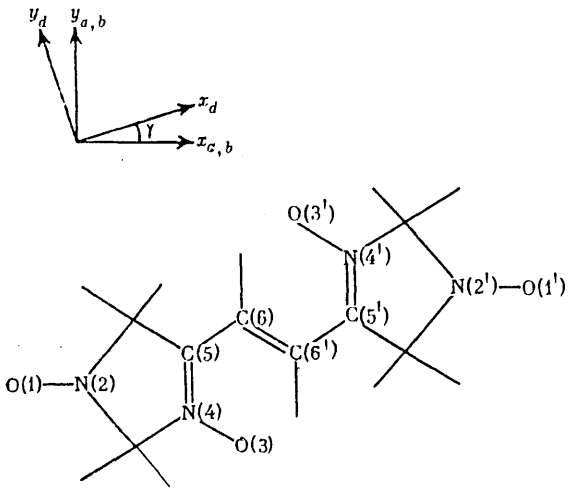


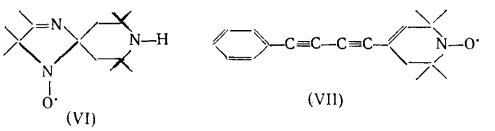
Figure 15. The structure of the *trans*-bis(2,2,5,5-tetramethyl-3-oxo-3-imidazolin-1-oxy-4-yl)ethylene biradical. Above —the relative dispositions of the axes of the $D(x_d, y_d)$ and $g(x_{a,b}, y_{a,b})$-tensors[45].

As early as 1976, interesting possibilities for the employment of EPR spectra in the two-millimetre range in the study of molecular mobility were noted[37]: in the fully resolved z components of the spectra of probe nitroxy-radicals, it is easy to observe the broadening (Fig.16) in which the frequencies of molecular movements in the range 10^7–10^8 s^{-1} can be determined directly (in the centimetre range a complex calculation of the line form is usually needed for this purpose. We shall consider the studies whose results demonstrate new, compared with the centimetre range, qualitative and quantitative possibilities for the employment of the millimetre EPR range. Studies of the anisotropy of the rotational lines are particularly instructive in this respect.

The procedure for the analysis of the anisotropy of the rotation developed for the EPR spectra in the three-centimetre range are more suitable for the region of rapid movements[47]. The knowledge of much more accurate values of all the magnetic parameters of the probe radical proved important under these conditions. In the previous Section it was shown that a realistic possibility for the determination of such data arises only in EPR measurements in the millimetre range. Thus progress in the determination of the magnetic parameters of nitroxy-radicals with the aid of millimetre EPR can serve as a basis for extensive studies of the anisotropy of rapid rotations in the centimetre range.

In the region of slow movements the manifestation of the anisotropy of the rotation leads to non-specific changes in the spectra in the 3-cm range[48] whose employment for the determination of the anistropy is difficult. On the other hand, in the millimetre EPR there is an entirely realistic possibility for the investigation of the anisotropy of the rotation precisely in the region of slow movements and important conclusions about the nature of the rotation (the presence of anisotropy, the direction of the preferential rotation axis) can be obtained directly from experimental data without resorting to a complex analysis of the spectra.

Radicals with different shapes, namely elongated[(VI) and (VII)] and nearly spherical [(V)], have been selected[49] for the study of the anistropy of the rotation of nitroxy-radicals in viscous matrices (liquid paraffin, vitrified toluene, etc.):



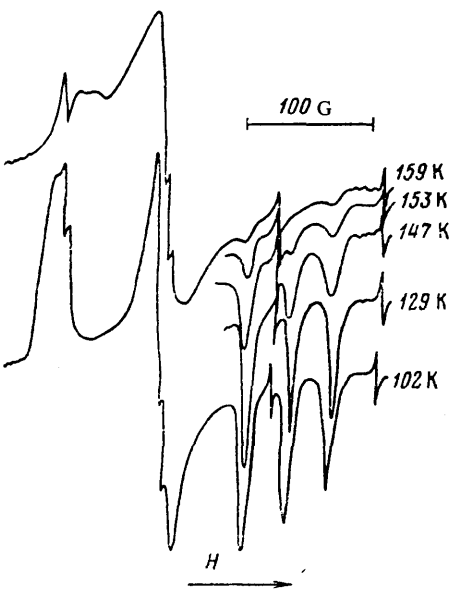


Figure 16. EPR spectra of radical (V) in a solution of polystyrene in toluene (15%) at different temperatures in the 2-mm range.

Furthermore, the long axes of radicals (VI) and (VII) are oriented in different ways relative to the principal axes of the g-tensor of the radical fragment. The direction of the long axis of radical (VII) is close to that of the x axis of the g-tensor, while radical (VI) direction of this axis is close to

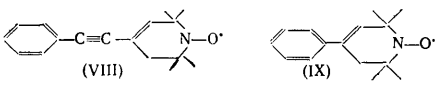
that of the y axis. Fig.17 shows how the EPR spectra of the chosen radicals vary when the rotational mobility of the probes is "unfrozen" with the increase of temperature. The spectra were recorded in the two-millimeter range at 100–350 K. Fig.17 shows that the relaxation changes, manifested primarily in the broadening and displacement of the components of the spectrum, begin at lower temperatures for radical (VI) and are characterised by a greater depth for the x and z components than for the y component.

The effect described has a simple qualitative explanation. For species with anisotropic magnetic parameters, different resonance frequencies correspond to different orientations in an extermal magnetic field. Rotation of the species leads to exchange between states with different resonance frequencies, which induces relaxation changes in the spectrum. However, each rotation is not involved in such exchange with identical efficiency. In particular, the rotation of the molecule about the axis directed along the magnetic field does not alter the angle between the field and the axes of the g- and A-tensors, i.e. does not affect the resonance frequency. For the "ellipsoidal" radicals distributed isotropically in the specimen, the axis of rotation in some of the centres is oriented along the field and no relaxation changes are manifested in the EPR signals corresponding to these centres. In the case of radicals (VI) the species oriented with the y axis of the g-tensor along the field satisfy this condition. These species in fact give rise to the y component of the EPR spectra, which does not therefore exhibit relaxation changes whatever the changes in the other parts of the spectrum—the x and z components. Only on further increase of temperature, when movements giving rise to a reorientation of the direction of the long axis of the radical are fairly effective, does the y component begin to participate in the frequency exchange.

The anisotropy of rotation is manifested to an even greater extent in the spectra of radical (VII) which has a somewhat more extended shape. Here rotation takes place preferentially about the x axis of the g-tensor and it can be seen from Fig.17 that the x component of the spectrum is incorporated in the relaxation process significantly later than the y and z components. The longitudinal ($\nu_\parallel$) and tranverse ($\nu_\perp$) frequencies of the rotational correlation then differ so much that complete averaging of the spectral y and z components as far as the "exchange-narrowed" triplet is attained and the spectrum assumes the form characteristic of the axial symmetry of the A- and g-tensors. As in the case of radical (VI), further heating leads to the broadening of the parallel x component and the perpendicular components and to their displacement towards the centre of gravity of the spectrum.

In the spectra of radical (V) relaxation changes are observed simultaneously and to an equal extent for all three canonical components. In this case there is apparently no separate axis of preferred rotations, in agreement with the approximately spherical shape of the radical.

The influence of the matrix on the degree of anisotropy of the rotation of the probe was investigated in greater detail in a study[50] where the spectra were analysed within the framework of the model involving changes in the orientation of the molecule in jumps by uncorrelated angles[51]. It was shown[50] that in the region of "slow" movements the effect reduces to a broadening of the canonical components of the spectrum equivalent to the convolution of the initial line form with a Lorentzian line whose width is different for different components in anisotropic rotation. Thus, in rotation about the x axis of the g-tensor of the radical fragment along which radicals (VII), (VIII), and (IX) are extended, i.e.



the y and z components are convoluted with a Lorentzian line having a width

$$\delta_L = 1/\gamma\tau_\parallel + 1/\gamma\tau_\perp$$

and the x component is convoluted with a line having a width

$$\delta_L = 2/\gamma\tau_\perp ,$$

where $\tau_\parallel$ and $\tau_\perp$ are the correlation times of the axially symmetrical movement about the long and short axes of the probe respectively and γ is the gyromagnetic ratio.

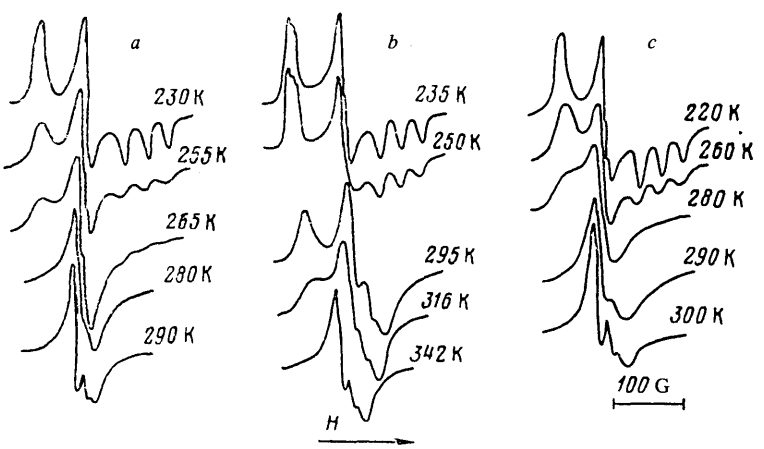


Figure 17. EPR spectra of solutions of the nitroxy-radicals (VI) (*a*), (VII) (*b*), and (V) (*c*) in liquid paraffin at different temperatures in the 2-mm range[49].

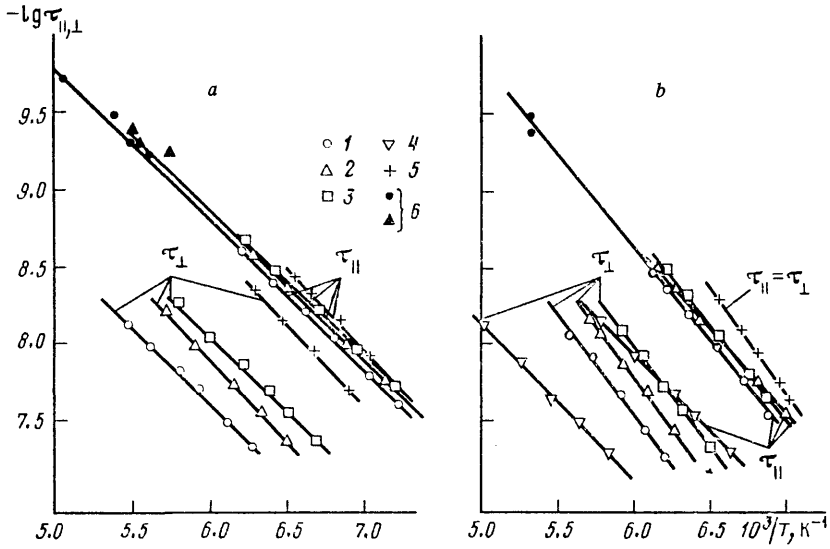


Figure 18. Arrhenius relations for the rotational correlation times of the radicals: *a*) in methanol; *b*) in toluene; *1*) radical (VII); *2*) radical (VIII); *3*) radical (IX); *4*) radical (X); *5*) radical (I); *6*) measurements based on the exchange-narrowed triplet[50].

If the rotation of the probe was sufficiently anisotropic and a resolved triplet was formed as a result of the averaging of the *y* and *z* components of the spectrum, the correlation times $\tau_\parallel$ and $\tau_\perp$ were determined from the formulae

$$\delta_L^\parallel = 2/\gamma\tau_\perp$$

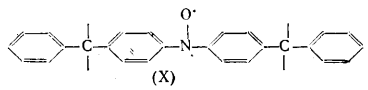
$$\delta_L^\perp = 2/\gamma\tau_\perp + \gamma(\Delta H_m)^2\tau_\parallel/8$$

for the parallel and perpendicular components respectively, where

$$\Delta H_m = g_0 H_0(1/g_{zz} - 1/g_{yy}) + m(A_{zz} - A_{yy});$$

$m = -1$, 0, +1 is the projection of the nuclear spin of nitrogen onto the magnetic field. Alcohols, (methyl, propyl, isodecyl, and isopentyl), toluene, liquid paraffin, and *p*-methoxybenzylidene-*p'*-butylaniline (MBBA) were chosen as the solvents.

Fig.18 presents the Arrhenius temperature variations of $\tau_\parallel$ and $\gamma_\perp$ for solutions of the radicals in toluene and methanol (in other solvents the relations were analogous). Over the entire range of measurements, the relations are linear. Fig.18 shows that a decrease of the length of the radical leads to a considerable (by a factor up to three) shortening of the time $\tau_\perp$. The time $\tau_\parallel$ for the same series of radicals diminishes by only 20%. For the radical



(X)

whose transverse dimension is greater than that of the radicals (VII)–(IX) and (V) and is close to the longitudinal dimension of radical (VIII), the variation of $\tau_\parallel$(X) is also close to that of $\tau_\perp$(VIII).

Thus the relations between the correlation times $\tau_\parallel$ and $\tau_\perp$ for different radicals in the same solvent are determined mainly by the dimensions of the radicals and $\tau_\parallel$ is influenced by the transverse dimension of the radical, while $\tau_\perp$ is influenced by its length.

The anisotropy parameters ($N = \tau_\perp/\tau_\parallel$) were measured for all the radicals at the temperature corresponding to the same $\tau_\parallel = 2\times10^{-9}$ s. The choice of this temperature was dictated by the fact that in its vicinity it is possible to determine simultaneously $\tau_\parallel$ and $\tau_\perp$ from the rotational broadening of the spectra. It was found that the anisotropy parameters *N* are either independent of temperature or decrease somewhat as the temperature is raised. However, the $N(T)$ relation could not be elucidated accurately, because the correlation times could be measured only over an inadequately wide temperature range. It was found that the anisotropy parameters depend greatly on the solvent and on the shape of the radicals. For example, in the series of alcohols *N* diminishes with increasing molecular weight of the alcohol: for radical (VIII), $N = 11.7$ in methanol and $N = 7$ in decyl alcohol. The lowest anisotropy parameters have been obtained for MBBA ($N = 5.7$) at temperatures below the region of its liquid-crystal state. A correlation with the parameters for different radicals in different solvents has been observed: firstly, the more extended molecule the greater the anistropy of its rotation in the given solvent and, secondly, if the anisotropy parameter of any one radical is greater in one solvent than in another, then an analogous relation is observed also for other radicals. The dependence of *N* on the properties of the radical and the solvent has been represented[50] by the empirical formula

$$N = KN_0, \qquad (4)$$

where N_0 is a parameter characterising the radical and depending solely on its geometrical dimensions; *K* is a parameter characterising the solvent for extended radicals; for spherical radicals, $N = 1$. Fig.19 illustrates the linear correlation between *N* and *K* in accordance with Eqn.(4). In order to account for the experimental data obtained, certain models of motion were examined[50] and it was shown that the model involving the "flickering of the free volume" yields the best agreement with experiment.

Another example of the study of the anisotropy of rotations in the millimetre range has been published by Grinberg et al.[44] They investigated the middle and terminal peroxy-radicals in polytetrafluoroethylene. In previous studies it had been found from three-centimetre[52] and eight-millimetre[53] data that the middle radical rotates as a rigid rotator in the vicinity of 300 K and that the axis of rotation is approximately perpendicular to the O–O bond. In the two-millimetre EPR range, not only all three principal values of the g-tensor but also the effective values of $g_\parallel$ and $g_\perp$ can be measured accurately by virtue of the full resolution of the components (Figs.3 and 11). The values of $g_\parallel$ and $g_\perp$ characterise the spectrum of the middle radical on partial averaging of the initial anisotropy to give cylindrical symmetry as a result of the rapid rotations about the axis of the rotator. The possibility of the accurate measurement of these parameters enabled the authors[44] to establish finally the disposition of the axis of rotation of the middle radical (the axis of the polymer chain) relative to the principal axes of the g-tensor. It was also found that, for the terminal peroxy-radicals the PTFE in the region of rapid movements (above 290 K), there is likewise no complete averaging of the spectra to give an isotropic singlet. It is noteworthy that these spectra (Fig.20) do not reduce either to the doublet characteristic of monoaxial rotation with the components $g_\parallel$ and $g_\perp$ (of the type shown in Fig.11), but consist of a set of such doublets with different parameters and statistical weighting factors. Thus it was possible to observe not only a definite "constraint" of the movement of the terminal groups at the polymer chain, leading to the anistropy of the rotation of the terminal RO_2 groups, but also the presence of a set of different structures of this fragment.

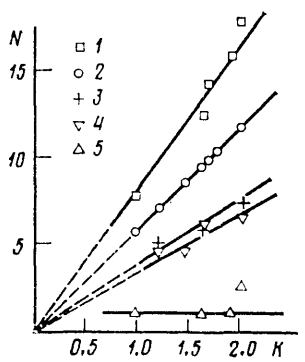


Figure 19. Dependence of the anisotropy parameter for different radicals on the solvent; radical: *1*) (VII); *2*) (VIII); *3*) (X); *4*) (IX); *5*) (I).[50]

A certain distribution of properties is in general characteristic of condensed media. In particular, molecular mobility can be inhomogeneous, i.e. characterised by a distribution with respect to rotational correlation times. The influence of kinetic inhomogeneity on chemical processes is well known[54,55] and procedures for its description have been adequately developed. There exist data concerning the manifestation of multiple frequencies of molecular rotations and the relaxation changes in the EPR spectra, but analysis is extremely difficult. The point is that even in the simple case of motion with a single correlation time, the changes in the spectrum are extremely complex, so that, for example, the determination of τ_c does not reduce (except in the region of rapid rotations) to the measurement of simple spectral parameters and it is in fact necessary to carry out a full synthesis of the spectrum and to compare it with experiment.

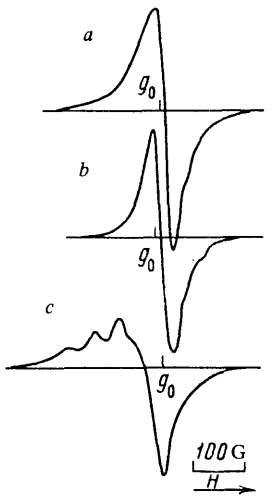


Figure 20. EPR spectra of terminal peroxy-radicals in the isotropic (*a*) and oriented by stretching (*b*,*c*) polytetrafluoroethylene specimens. The extension axis is parallel to the field at 300 K (*c*) or is perpendicular to the field (*b*); g_0—signal of the reference standard[44].

If one considers in addition the influence on the spectrum of the anisotropy of the rotation of the dynamic model of motion (diffusion, jump, or free rotation[56]), then the problem of the determination of the parameters of the distribution with respect to the correlation times of the molecular movement of the radicals from the EPR spectra in the three-centimetre range becomes virtually insoluble. Progress can be made in this field only in special cases of the so called "isolated", i.e. well resolved from the remainder of the spectrum, components. If the movement of the paramagnetic centre induces the frequency exchange of this component with the spectrum, the changes reduce simply to a broadening linear in terms of the exchange frequency and to its shift to an extent for which its overlap with other parts of the spectrum begins. An example of such components can be provided by the forbidden $\Delta M_S = 2$ transitions in radical dimers, on the basis of the spectra of which it proved possible[57,58] to establish the presence of distributions with respect to the correlation times and to determine the parameters of the distribution. Another example may be the canonical components in the spectra characterised by the anisotropy of the magnetic parameters. Since the effectiveness of the employment of these components in order to characterise the movement depends on the degree of their resolution, the best results can be obtained in the millimetre EPR range.

Such analysis of the relaxation changes of the x component of the spectrum (Fig.3) of the middle peroxy-radical in polytetrafluoroethylene as a function of temperature has been carried out[44]. The decrease of the amplitude of the x component is far in advance of its broadening, i.e. the integral

intensity diminishes, which is inconsistent with the hypothesis that relaxation processes influence spectra of this type. According to calculations[59], the changes in the canonical components of the anisotropic spectra reduce, as already mentioned, to their broadening and displacements and, so long as the component is observed as an isolated component, i.e. the overlap with the neighbouring components has not begun, its integral intensity remains unaltered. The decrease of the integral intensity of the x component observed in the case under consideration can be induced by the scatter of the values of τ_C in the specimen, so that the component for some of the radicals characterised by short τ_C is greatly broadened and is not recorded.

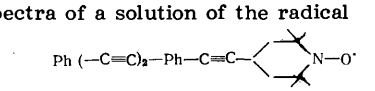
The analysis of the decrease of the intensity of the x component with increase of temperature[44] established the distribution with respect to the activation energies for the movement of the radical and led to the determination of the parameters of this distribution. It must be specially emphasised that, whereas the data obtained previously for the inhomogeneity of the molecular mobility referred to movements involving different types of rotation, in the given instance one is dealing with rotations of a rigorously defined type—about the axis of the polymer chain.

The anisotropy of the rotational mobility is frequently accompanied by the orientational order of the molecules in the specimen. The character of the rotation of the probe molecule is determined by the structure of its immediate environment—the structure of the "cell" in which it is placed. The cell follows to some extent the shape of the probe and is elongated for an elongated species. The probe is oriented preferentially along the long axis of the chain. If the specimen as a whole is disordered, the cells are distributed isotropically. However, the specimen can be also non-isotropic—for example, it can consist of extended polymers, liquid crystals in external fields deposited on the support of the system, etc. In such cases the angular distribution of the probes is also non-isotropic, which is manifested in their EPR spectra.

The possiblity of the analysis of the angular distribution of the radicals on the basis of EPR spectra depends on the anisotropy of their magnetic-resonance parameters, i.e. on the extent to which the resonance fields for different orientations of the radical relative to the direction of the magnetic field of the spectrometer are different. The data presented in the preceding Sections show that only in the millimetre EPR range it is possible to achieve the optimum conditions for the investigation of the anisotropy of the distribution of the nitroxy-radicals widely used as probes and labels as well as peroxy-radicals for which the ~O–O· fragment can be regarded as a paramagnetic label on the "body" of the molecule.

We considered above, in relation to the study of Grinberg et al.[44], how the orientation of PTFE molecules by the stretching of the polymer is manifested in the EPR spectra of peroxy-radicals in the 2-mm range (Figs.12 and 20). It must be emphasised that an increase of the spectral resolution did in fact permit in the given instance a detailed description of the structure of the radical centre (Fig.12) and the differentiation of the individual structures of chemically equivalent radicals.

The study of the orientational order of nitroxy-radicals in the millimetre EPR range is very promising[60]. Fig.2 presents the spectra of a solution of the radical



in MBBA at different temperatures of the measurement. The compound MBBA is characterised by the presence of a nematic phase in the range 290–318 K. The spectrum (Fig.21*a*) of the isotropic liquid phase (above 318 K) has a structure characteristic of the axial symmetry of the g- and A-tensors and corresponds to probes rapidly rotating around the long x axis of the radical ($g \cong g_{xx}$) and the directions of the x axes are distributed isotropically (analogously to Fig.17*b*). On passing to the nematic phase (Fig.21*b*), the spectrum is localised in the vicinity of the resonance field corresponding to the orientation of the radical with the x axis along the direction of the field. Thus the orientation of the domains of the nematic MBBA in the magnetic field leads to a pronounced (almost complete) orientation of the "cells" containing the probe. This structure of the matrix can be "frozen" by the rapid cooling of MBBA to below 250 K. Fig.21*c* presents the spectrum of the frozen specimen, which is close to the spectrum in Fig.21*b*.

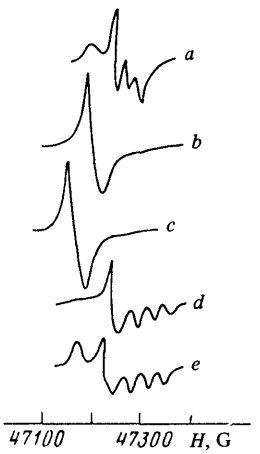


Figure 21. EPR spectra of a solution of nitroxy-radicals in MBBA in the 2-mm range. Temperature of the measurement (K): *a*) 320; *b*) 290; *c*)–*e*) 200; *c*) specimen of the nematic phase frozen at 200 K in the field of the spectrometer; *d*) specimen *c* frozen outside the field of the spectrometer; *e*) frozen specimen of the isotropic MBBA phase.

Ordering in the nematic MBBA phase can be induced also under the influence of the walls of the bulb. If the specimen (quartz capillary with an internal diameter of 0.5 mm) is kept at 300 K, is rapidly frozen outside the field, and the EPR is recorded without raising the temperature, then the corresponding spectrum (Fig.21*d*) does not contain the x components, which corresponds to a distribution of the radicals with the x axis preferentially perpendicular to the field [the axis of the bulb in the spectrometer (Fig.1) is perpendicular to the axis of the solenoid]. Freezing of an isotropic phase specimen leads to the spectrum illustrated in Fig.21*e*, which corresponds to a random distribution of the radicals. The loss of orientational order is also observed in frozen specimens subjected to preliminary orientation under the influence of the field of the spectrometer or the walls of the bulb. Under these conditions, in the initial spectrum of the type illustrated in Fig.21*c* the y and z components appear and increase in intensity, the intensity of the x component falls, and in the limit the spectrum tends to the form shown in Fig.21*e*. Such randomisation apparently corresponds to a transition from the vitrified structure of the liquid crystal to the polycrystalline form and is extremely slow (tens of minutes at 250 K).

The example considered demonstrates the possibilities of the millimetre EPR range in the study of the angular distribution of radicals and the factors leading to the establishment and loss of orientational order in the substance.

Whereas in the case of slow molecular movements, the millimetre EPR makes it possible to obtain different qualitative characteristics of the movements of radicals, in the case of rapid movements such EPR permits a considerable expansion of the range of the measured correlation times. In the region of small values of τ_c the components of the spectrum occupy positions defined by the isotropic (averaged as a result of rotation) values of the magnetic parameters and the widths contain a contribution "incompletely averaged" by the movement. Thus in the simplest case of the frequency exchange between the components of a doublet with a 1:1 intensity ratio separated by a frequency interval $\Delta\omega$, the residual broadening is[61]

$$\delta H \simeq (\Delta\omega)^2\tau_c/\gamma \ .$$

The expresson for δH relating to spectra with anisotropic parameters can be more complex (see Chapter III in Berlinger's book[39]), but here too the residual broadening is greater the greater the initial extent of the spectrum in the limit corresponding to slow molecular movements. The range of the averaged frequencies then increases with increase of the polarising field owing to the contribution determined by the anisotropy of the g-factor ($\Delta\omega \cong \gamma\Delta g H_0$), so that complete averaging in the spectra in the millimetre range requires higher frequencies of the movement than in the 3-cm range.

The limits within which τ_c is accessible to measurement which are attainable in the 3-cm and 2-mm ranges have been compared[62]. It was shown that, on the side of rapid movements, the boundary of the measured correlation times shifts from 6×10^{-11} to 4×10^{-12} s on passing from the three-centimetre range to the two-millimetre range. The above values change somewhat when the matrix is replaced or when the structure of the probe is altered as a result of a change in the limiting (not averaged by rotation) line width, but the overall effect of the transition to the 2-mm range (amounting to more than an order of magnitude) is preserved.

V. CONCLUSION

The results presented above, obtained with the aid of EPR in the two-millimetre range, demonstrate, in the present authors' view, the possibility of obtaining qualitatively new information in fields such as the metrology of free radicals, the study of molecular mobility, the study of the electronic and geometrical structures of radicals and biradicals, the study of matrix effects, etc. It is important to note that the qualitative leap forward is due to the appearance of the possibility of measuring electron spin resonance in strong fields over a wide temperature range and in objects of different types, characteristic of both chemistry and biology. All the advances enumerated above are associated with the increase of the resolving power of the method. The relative increase of frequency on passing from the 8-mm range, adopted for a long time, to the 2-mm range does not exceed the increase of the frequency on passing from the 3-cm to the 8-mm range, but experiment confirmed the estimates presented at the beginning of this review, according to which conditions leading to a high resolution of the spectra of typical organic free radicals occur precisely in the wavelength range shorter than 3 mm. This makes it possible to regard the EPR spectroscopy in the two-millimetre range as a method for the investigation of free radicals which has a high resolving power with respect to the g-factors. Apart from the applications already tested, one may specify a series of further applications whose likely usefulness follows from the parmeters attained in the EPR in the millimetre range.

The high absolute sensitivity ($\sim5\times10^7$ spin G^{-1}) can be used for the investigation of micro-objects. With this sensitivity, it is easy to show by calculation that the signal due to 10^{-13} g of the stable DPPH radicals can be recorded. If a spin-labelled object with a concentration of the usual spin labels of 10^{-5} mole cm^{-3} is used, then a specimen with a linear dimension of 2–3 μm can be used to measure the spectrum, i.e. in principle there is a possibility of investigating individual living cells, etc. For ferromagnetic particles with a narrow ferromagnetic resonance line, the lower limit of the size of the specimen may be only 10^{-15} cm^3.

The high absolute sensitivity combined with a high resolution with respect to the g-factor, which makes it possible to detect the perturbations induced by weak intra-electronic and interelectronic interactions, makes it possible, in principle, to use the EPR millimetre range for microchemical analysis using stable radicals as specific reagents. The high absolute sensitivity and also the high sensitivity to the angular orientation of the paramagnetic centre in the presence of the anisotropy of the g-factor make EPR in strong fields a promising procedure for tomography (zeugmatography) of small objects with a higher spatial resolution than in NMR or EPR in the centimetre range. Estimates have shown that in favourable situations (high concentrations, narrow lines) the spatial resolution can reach 0.1–1 μm.

The suppression of forbidden transitions and the weakening of the interaction between the individual resonances make EPR in intense fields a convenient method for the investigation of the relaxation effects, transmission effects, and the transfer of saturation.

Thus by no means all the possibilities inherent in the EPR spectroscopy of the two-millimetre range have been so far realised. All this gives rise to the hope that greater sophistication of the experimental technique associated with the transition to the range of millimetre wavelengths will be justified by the increase of the amount of information derivable from the measurements and the expansion of the applications of the EPR method.

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Electron Spin Echo Study of the Steric Characteristics of the Formation and Reactions of Radicals in a Solid Phase

Yu.D.Tsvetkov

The general characteristics of electron spin echo (ESE) spectrometers are considered. A Soviet spectrometer and certain foreign instruments used in physicochemical research are described. The fundamental postulates and results of the theory of magnetic dipole-dipole interactions are briefly formulated in relation to the analysis of the results obtained by the ESE method.
Studies by the ESE method of the steric characteristics of chemical reactions in solids are surveyed. Investigations of the structures of radical tracks in irradiated organic and inorganic systems are considered and it is shown that data concerning the pair distribution function with respect to distances in ion—radical pairs can be obtained by the relaxation probe method and the method of double electron—electron resonance in ESE spectroscopy. The principal results of the investigation of the pair distribution in the formation of radicals under the influence of ultraviolet light and γ-rays as well as the changes in the pair distribution in the course of diffusion and reactions of free radicals and atoms in frozen glasses are discussed.
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I. INTRODUCTION

The development of UHF techniques in recent years makes pulsed EPR methods increasingly available for various physicochemical applications. Among these procedures, the electron spin echo (ESE) method—a special pulse variant of EPR, analogous in its experimental formulation to pulsed echo methods in NMR spectroscopy[1,2]—has developed extensively. In this method, under $\omega_0 = \gamma H_0$ resonance conditions (γ is the gyromagnetic ratio for the electron and H_0 the external magnetic field), the spin system is acted upon by a series of UHF pulses and the spontaneous emission from the system—the spin echo signal—is investigated (Fig.1). In the two-pulse variant of the excitation, the primary echo is produced, while in the three-pulse variant a stimulated echo is produced. The first 90° UHF pulse gives rise to a coherent state of the spin system, which is correlated as regards initial phase. The break up of this state into individual "isochromatic components" in the $xy \perp \mathbf{H}_0$ plane of the coordinate system, rotating at a frequency ω_0 about the z axis, is caused by phase relaxation (transverse) processes (with a time T_2) and the restoration of the magnetisation to the equilibrium value M_0 along the $z \parallel \mathbf{H}_0$ axis is due to the spin-lattice relaxation (longitudinal) with a characteristic time T_1. A 180° pulse applied at a time interval τ reverses the movement of the isochromatic component, which gives rise to the echo signal at time 2τ. The signal amplitude $V(2\tau)$ diminishes as the time interval τ between the UHF pulses is altered.

The spin echo for paramagnetic species was first observed by Blume[3,4] (USA) in a study of solutions of sodium in liquid ammonia. The ESE theory has been at present developed in fair detail[5-7]. For physicochemical applications, the following characteristics of the ESE method must be noted.

1. Compared with the stationary EPR method, which constitutes a frequency domain spectroscopy, ESE is a time domain spectroscopy in which the times of the evolution of the spin system (T_1, T_2) are recorded directly.

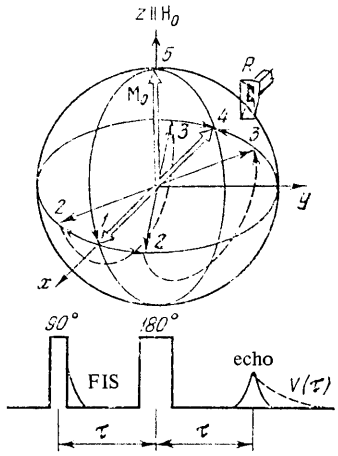


Figure 1. The vector model of the generation of a spin echo signal; a 90° pulse rotates the magnetisation vector $\mathbf{M}_0$ in the xy plane (*1*); decomposition of $\mathbf{M}_0$ into isochromatic components at a rate T_2^{-1} (*2*) inducing a free induction signal (FIS) in the receiver (*R*); rotation of the isochromatic components by an 180° pulse (*3*); restoration of $\mathbf{M}_0$ along the x direction (*4*)—the generation of the echo signal; restoration of $\mathbf{M}_0$ along the z direction as a result of the spin–lattice relaxation at a rate T_1^{-1}; τ—time between pulses; $V(\tau)$—decay of the echo signal as τ is altered.

2. The possibility of obtaining the ESE signal (the break up of the overall magnetisation vector $\mathbf{M}_0$ into isochromatic components and its subsequent restoration) arises via a mechanism involving the static inhomogeneous broadening of the EPR line, while the kinetics of the decrease of the LSE

signal $V(2\tau)$ with increase of the time interval between the UHF pulses, i.e. the form of the relation, contain information about the different time-dependent stochastic processes in the spin system. These processes also arise as a consequence of magnetic interactions such as magnetic dipolar (electron–electron and electron–nucleus) or exchange interactions. Thus ESE makes it possible to investigate magnetic interactions under conditions uncomplicated by the inhomogeneous static line broadening of the kind which occurs in the stationary EPR.

3. The magnetic interactions in the spin system lead in addition to the modulation of the relaxation decay of the ESE signal. The Fourier transformation of the modulated decrease yields the frequencies and amplitudes of the magnetic interactions. A unique feature of ESE is the possibility of analysing relatively weak hyperfine and quadrupole interactions in polyoriented systems, which creates a basis for structural applications of the method.

4. As a pulsed variant of EPR spectroscopy, ESE can be conveniently combined with various physical and specially pulsed influences on the test system. There exist kinetic variants of ESE in which paramagnetic species are generated by light[8], a laser pulse[9], or a fast electron pulse[10]. Methods in which the system is acted upon by electric field pulses have been developed[11].

In the present review we shall consider only one of the fields of the physicochemical applications of the ESE method—studies of the steric characteristics of the formation and reactions of free radicals, atoms, and ions in solids. These investigations are based on measurements for magnetic dipole–dipole interactions. They were begun at the Institute of Chemical Kinetics and Combustion of the Siberian Division of the USSR Academy of Sciences in 1965 on the initiative of Acad.V.V.Voevodskii. Reviews of the early results may be found in other publications[6,7,12].

II. ELECTRON SPIN ECHO SPECTROMETERS

Approximately 30 ESE spectrometers are actually working or are in the adjustment stage in various laboratories throughout the world. In foreign laboratories the spectrometers are as a rule assembled from separate units purchased from various firms. In contrast to the first models[6,13,14], the instruments constructed nowadays are coherent ESE spectrometers, which implies that, for a fixed phase of the exciting UHF pulses, the phase of the detected ESE signal is also known. A coherent spectrometer is more sensitive than an incoherent one and has a linear characteristic—the change in the amplitude of the detected signal is proportional to the amplitude of the signal applied to the input of the detector. In addition, there is a possibility of direct measurements of the polarisation of the ESE signal, which arises in various chemical reactions, i.e. the phenomenon of the electronic polarisation of the spins[15].

The ESE signal arises when the spin system is acted upon by a series of UHF pulses which rotate the vector $\mathbf{M}_0$ through a definite angle θ. In the two-pulse variant of the excitation, the amplitude of the echo signal is determined by the angles θ_1 and θ_2:

$$V = V(2\tau)\sin\theta_1 \sin^2\frac{\theta_2}{2}$$

$$\theta_{1,2} = \gamma H_1 \tau_{p_{1,2}}$$

where H_1 is the amplitude of the UHF pulse and τ_p its duration. The duration of the pulses in experiments designed to investigate the phase or spin–lattice relaxation must be much shorter than T_1 and T_2. The times T_1, $T_2 \cong 10^{-7}$ s are nowadays of practical interest, so that we must have $\tau_p \cong 2 \times 10^{-8}$ s, which yields $H_1 \cong 5$ G for $\theta = 90°$. Such a strength of the UHF magnetic field is ensured by a source with a pulse power $P_p \cong 1$ kW.[6] Naturally one can employ also less powerful sources for the excitation of the ESE signal. However, one must then bear in mind that, for small H_1, the signal amplitude diminishes in proportion to H_1^3. Furthermore, for a whole series of experiments, including studies of the dipolar interactions and modulation phenomena, one must excite at least a major portion of the EPR spectrum if not the entire spectrum with a width ΔH, i.e. it is necessary that the condition $H_1 \cong \Delta H$ should hold. In general purpose ESE spectrometers the power of the pulses from the exciting source is therefore as a rule ~1 kW.

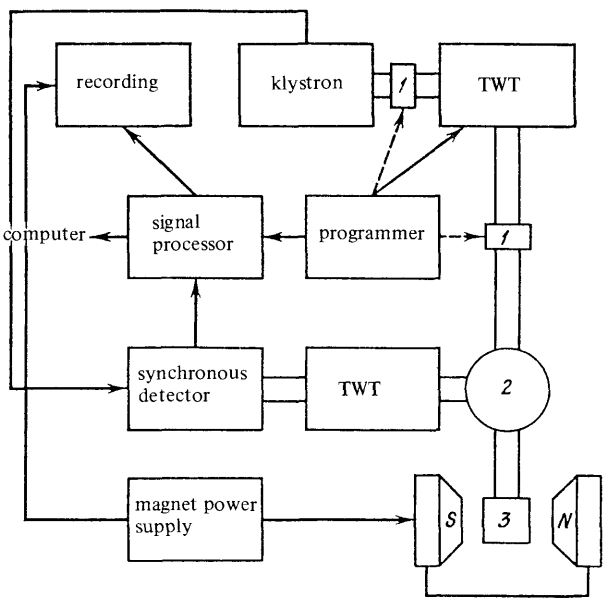


Figure 2. Generalised block schematic of an ESE spectrometer: 1) UHF switch; 2) circulator; 3) cavity; TWT—travelling wave tubes.

A block schematic of a spectrometer for the 3-cm wavelength range is illustrated in a general form in Fig. 2. One or several travelling wave tubes (TWT), which function as amplifiers of the power of the triggering klystron, are usually employed as a source of the UHF pulses; the UHF part of the spectrometer contains standard elements for EPR spectroscopy: attenuators, circulators, phase inverters, and switches. In contrast to EPR spectroscopy, the cavity need not have a high Q factor (see below). Apart from the additional frequency tuning, provision is usually made for reducing the Q factor by introducing an absorbing element such as a carbon or ferrite plate at the antinode of the electric field. Before it reaches the synchronous (balanced) detector, the signal is additionally amplified with the aid of special low-noise and low-inertia TWT. Beyond the detector, the signal in the form of a pulse enters the interpretation unit, which incorporates elements transforming the signal into a digital form, a signal accumulation system, and a system for its treatment in order to suppress noise. In a digital

or analogue form, the signal is applied to the recording device—a pen recorder, a perforated tape, another digital indicator, or a computer.

The most important element of the ESE spectrometer is a programmable pulse sequence generator. By controlling the TWT or UHF switches, it ensures the formation of a train of UHF pulses, determines their duration τ_p, the intervals between the pulses, and the time scan of these intervals as well as the frequency of the repetition of a series of pulses, and controls the signal treatment unit of the recording unit. Finally, each spectrometer contains a scanning unit and a unit for the calibration of the permanent magnetic field H_0.

According to theoretical estimates[6], the sensitivity of the ideal coherent ESE spectrometer is in the range 10^{10}–10^{11} spins in the specimen for a phase relaxation time $T_2 = 3 \times 10^{-7}$ s, a spin–lattice relaxation time $T_1 = 3 \times 10^{-6}$–10^{-4} s, and a signal recording time of 1 s, which corresponds to the sensitivity of modern stationary EPR spectrometers. An increase of sensitivity can be achieved by increasing the recording time as a result of the increased number of accumulations. We may note that, so far as we are aware, measurements of the sensitivity of ESE spectrometers, necessary for comparison with calculated values, are not available in the literature.

For any time domain spectroscopy, the most significant parameter of the ESE spectrometer is its resolving power with respect to time. This parameter should be understood as the minimum relaxation time, for example, the phase relaxation time T_2 recorded by the spectrometer ($T_{2,\min}$). For an ideal spectrometer, on excitation with a train of 90–180° pulses with durations τ_p and $2\tau_p$, we have

$$T_{2,\min}^{id} \geqslant 3\tau_p$$

In the case of a real spectrometer there is in addition a significant contribution by the so-called "ringing" of the cavity. When a resonator is acted upon by pulses, a reflected signal is generated, whose rear front is represented by an exponential function decaying with a time constant $t_0 = Q/2\omega_0$. This signal overloads the UHF amplifier with respect to time[6]:

$$\tau_r = t_0 \ln P_p/pP_n$$

where P_p is the power of the UHF pulse, $P_n = kT\omega_0/2Q$ the power of the noise, and p the amplification factor. Thus the minimum time T_2 which can be recorded by the spectrometer increases by an amount τ_r:

$$T_{2,\min} \geqslant 3\tau_p + \tau_r .$$

For $P_p = 1$ kW, $Q = 500$ $T = 300$, and $p = 100$, this additional so-called "ringing" time or "dead" time of the spectrometer is approximately 120 ns. Taking into account the fact that commuting UHF devices nowadays have a fast response time of ~10–20 ns, the real resolving power of the spectrometer is 200–300 ns. More accurate estimates[5,6] yielded similar values. The simplest method for reducing $T_{2,\min}$, by decreasing Q to low values, is evidently inapplicable because the sensitivity of the spectrometer is proportional to $Q^{1/2}$.[5,6]

The coherent spectrometer of the Institute of Chemical Kinetics and Combustion of the Siberian Division of the USSR Academy of Sciences has been described in full detail in recent literature[16,17]. One of the characteristic features of this apparatus is the possibility of generating UHF pulses with a power up to 5 kW for a minimum duration of 20 ns, which is ensured by a magnetron operating with synthronisation of its frequency and phase by the UHF oscillations of an amplification cascade based on TWT; when only TWT are used, the power of the pulse is 1 kW. Another feature is the modulation of the UHF phase to suppress the signal due to the "ringing" of the cavity and to increase the time resolution. The ESE signal is excited at a specific frequency of the repetition of the "pulse (90°)–pulse (180°)–echo" cycles. If the phase of the first pulse is reversed in each even cycle, then the phase of the echo signal in the even cycles is also rotated by 180° compared with the phase of the signal in odd cycles. The "ringing" signal, which is independent of the phase of the pulses, is the same for even and odd cycles. By subtracting the signals from the even and odd cycles in the signal processor unit, it is possible to suppress the "ringing" signal. The resolving power of such a spectrometer is approximately 2×10^{-7} s.

The programmable pulse sequence generator (programmer) of the spectrometer generates a series of four pulses, one of which is used for external synchronisation and one is a strobe pulse. The duration of the pulses and the intervals between them are regulated in 1 ns steps. These intervals are varied automatically at specified steps and at a specified rate. The programmer also generates a pulse which rotates by 90° the UHF pulse and ensures the time scan of the pen recorder in the spectrometer.

The stability and convenience of the operation of the spectrometer are also ensured by a special device for the stabilisation of the field and its scan by means of an NMR transducer, which makes it possible to determine the field strength to within 3×10^{-4}% and to alter it at a specified rate in the specified range with continuous digital indication of the value of H_0.

A modified variant of the ESE spectrometer described previously[8], was examined briefly in another communication[19]. This spectrometer is used in the Bell Telephone Laboratories (USA). A TWT with a power up to 1 kW, controlled by a modulator, which is in its turn triggered by the programmable pulse sequence generator, is employed as the source of 20 ns UHF pulses. In the recording circuit there is a coherent receiver of the homodyne type with a videoamplifier, a strobe integrator, and a pen recorder. A novel cavity of the gap type, with a high filling factor and a small size, which is convenient for use at 4.2 K, is incorporated in the spectrometer. In the two-pulse variant, τ is varied over the range 0.14–2.4 μs during the recording of the decay of the ESE signal. A waveguide delay line, which makes it possible to diminish by ~30% the dead time of the spectrometer, has been described[20].

Trifunac et al.[21] described an ESE spectrometer for kinetic studies in pulse radiolysis (Argonne National Laboratory, USA). The source of the UHF pulses is a TWT with a power of 10 W, which amplifies the UHF pulses of the klystron generated with the aid of a fast-response (10 ns) switch. The 90° pulse then has a duration of 30–100 ns, and generates a field $H_1 \cong 1$ G in a cavity of the reflecting type. The circuit employs two further fast-response switches to protect the detecting section of the spectrometer from overload pulses. A low noise TWT or a unipolar amplifier based on field effect transitors can be used in the detector. A characteristic feature of the spectrometer is its employment together with a 3 MeV Van de Graaff accelerator, which makes it possible to irradiate the specimens by intense electron pulses lasting 5–100 ns with a current of ~2 A in the pulse. In a specimen having a volume of 10^{-4} litre, such pulses give rise to a radical concentration of ~10^{-3} M in aqueous media. In kinetic experiments the time interval between the electron pulse and the first 90° UHF pulse was varied. Remote control was used for the part of the apparatus located in the zone unprotected from the radiation, this incorporated the UHF system and control units as well as the permanent H_0 magnetic field unit.

It is known that problems associated with the signals from the bulbs or cuvettes containing the test specimen arise in radiation experiments using, for example, the stationary EPR method. A novel procedure for the reduction or even elimination of this signal has been proposed[21]. If the ESE spectrometer operates under signal detection conditions with inclusion of a radiation pulse (A) and without a pulse (B), then the phase of the B signal before accumulation can be inverted so that $A - B$ difference signals containing only the transient component of the EPR spectrum appear in the accumulator. An example of such an experiment has been presented[21] with the exclusion of the long-lived signal in quartz and the isolation of the spectral lines of the short-lived radical $\dot{C}H_2CO_2$-generated when a solution of potassium acetate is irradiated.

Among other spectrometers described in the literature and used at the present time in vigorous research, we shall mention the second instrument of the Argonne Laboratory[22], the analogous spectrometer at Cornell University (USA)[23], and the spectrometer at the University of Houston (USA)[24]. The ESE spectrometer at the Leyden University in Holland[25] is used to investigate triplet states, while in the University of Delft ESE spectrometers for both the 3 cm [26] and 8 cm [27] ranges are used to study modulation phenomena. The complete list of the spectrometers, some of their technical characteristics, and the main fields of the research carried out on them have been published[28].

III. MAGNETIC DIPOLE–DIPOLE INTERACTIONS IN ESE SPECTROSCOPY

The study of the spatial distribution of paramagnetic centres in solids is based on the theory of magnetic dipole–dipole interactions developed in relation to the ESE method. A review of the present state of the theory can be found in the literature[6,7,29,30]. We shall deal only with the results which are most significant for applications.

The surrounding spins k generate at the site of a given spin p a local field ΔH_p which depends on the relative positions of the spins in the lattice and on the changes in the orientation of the surrounding spins as a function of time. The shift of the resonance frequency of two spins $c/S = 1/2$ corresponding to this field is defined thus:

$$\Delta\omega_{pk}(t) = \gamma^2\hbar r_{pk}^{-3}(1 - 3\cos^2\theta_{pk})\, m_k(t) = A(r_{pk})\cdot m_k(t)\,,$$

where m_k is the projection of the spin k onto the direction of the external field H_0 and $\theta_{pk}$the angle between the vector $\mathbf{r}_{pk}$ and the field $\mathbf{H}_0$. For an assembly of spins k, the shifts are added together:

$$\Delta\omega_p(t) = \sum_k \Delta\omega_{pk}(t)\,.$$

The contribution of this interaction to the time-dependent decrease of the spin echo signal amplitude is defined by the relation

$$V(t) = V_0 \left\langle \exp\left[i \int_0^t S(t)\,\Delta\omega_p(t)\,dt \right] \right\rangle_t \Big\rangle_p\,,$$

where $S(t) = 1$ in the time interval $(0, \tau)$ and $S(t) = -1$ in the time interval $(\tau, 2\tau)$ in the two-pulse ESE variant. Averaging with respect to t is carried out over all the realisations of the time-dependent changes in $m_k(t)$ and the averaging with respect to p takes into account the spatial distribution of the spins k relative to the spins p. If there are only two spins p and k separated by a distance r_{pk}, then the contribution due to the dipole–dipole interaction for the spin k to the decrease of the ESE signal of the spin p must also be averaged with respect to time:

$$V_p(t) = \left\langle \exp\left[iA(r_{pk}) \int_0^t S(t)\, m_k(t)\, dt \right] \right\rangle_t\,.$$

The shift of the resonance frequencies of the spins changes as a function of time as a consequence of random spin flips. Such random changes in the resonance frequencies of the spins are called spectral diffusion. Two mechanisms of random spin flips are usually considered: the spin–lattice relaxation process in which the mutual orientation of the spins is altered (flip-flops). In the latter case the spin excitation migrates in space (there is spin diffusion). If the spin–lattice relaxation makes a definite contribution to the random changes in the resonance frequencies, such spin systems are referred to as type T_1 samples. If the spectral diffusion is induced by random spin flips in the course of spin diffusion, such systems are referred to as type T_2 samples.

Another mechanism of phase relaxation due to the dipole–dipole interaction is associated with a specific pulsed influence on the system of spins in the ESE method: a 180° pulse alters the orientation of the local ΔH_p field generated by the spins k, i.e. executes an "instantaneous" shift of the resonant frequency of the spins. This gives rise to relaxation via the so-called instantaneous diffusion mechanism. Even if the spectral diffusion is fully "frozen", the dipole–dipole interaction between the spins results in a decrease of the ESE signals via the instantaneous diffusion mechanism. If during the time of observation the spins k manage to alter their orientation in a random manner (as a result of spin–lattice relaxation or spin diffusion), they contribute to the decrease of the ESE signal via both instantaneous and spectral diffusion mechanisms. The contribution of the instantaneous diffusion mechanisms depends very greatly on the amplitude H_1 and the duration τ_p of the UHF pulses on the relation between the amplitude of the UHF field H_1 and the overall width and form of the EPR spectral line $[g(\omega)]$.

The random spin flips are described within the framework of various model time distributions. Either an identical average flip rate w is then assumed for all the spins or a distribution of the spins with respect to the flip rate is introduced, for example of the form

$$\varphi(W)\,dW = \left(\frac{3W_{\max}}{2\pi}\right)^{1/2} W^{-3/2} \exp\left(-\frac{3W_{\max}}{2W}\right) dW\,, \qquad (1)$$

where $W_{\max}$ is the most probable flip rate. Using such time distributions, the decrease of the ESE signal has been calculated for the model case of a uniform distribution of spins in space[29].

The paramagnetic centres can be distributed in the lattice of a solid either uniformly or non-uniformly. In the former case they can be stabilised with identical probabilities at any lattice site. For example, a distribution of this type has been observed in frozen vitreous dilute solutions of stable radicals or complexes of paramagnetic ions. The spatial distribution of the paramagnetic centres can be described with the aid of a pair distribution function for the particles $m(r)$, which characterises the probability of finding a paramagnetic centre at a distance r from a specified paramagnetic centre.

If the paramagnetic species are distributed in the specimen in pairs and the distribution with respect to distance within the pairs is specified by the function $n(r)$, then the decrease of the ESE signal is described by the expression

$$V(2\tau) = \int V_p(2\tau, r)\, n(r)\, d^3\mathbf{r}\,.$$

For a uniform distribution of species in the specimens with an average concentration c_{av}, we obtain[29]

$$V(2\tau) = \exp\left\{-c_{cp}\int d^3\mathbf{r}\,[1 - V_p(2\tau, r)]\right\}.$$

The problem of the description of the kinetics of the decay of the ESE signal due to magnetic dipole–dipole interactions of the species is solved in this way in the general case. As a rule, the solution for a wide range of times τ can be obtained only numerically. Hitherto, a wide range of model problems have been analysed in which the spatial distribution of the paramagnetic centres was varied and different types of random processes were employed to describe spectral diffusion[29,31].

The results for systems with a uniform distribution of paramagnetic species are of greatest practical value. For such systems, there is a possibility of a comparison with experiment. They serve as reference standards in the case of a non-uniform distribution of species. Calculation of the rate of decay of the ESE signal owing to the dipole–dipole interactions for a uniform distribution has been carried out for a single spin-flip rate W and for a distribution with respect to rates of type (1). In the latter case, the kinetic expression for example, assumes the form

$$V(2\tau) = \exp\left\{10^{-18}c_{cp}\left[Q_B(\tau, W_{max}) + \left\langle \sin^2\frac{\theta}{2}\right\rangle_{g(\omega)} Q_A(\tau, W_{max})\right]\right\},$$

where $\langle\ldots\rangle_{g(\omega)}$ denotes averaging with respect to the distribution $g(\omega)$ of the frequencies in the EPR spectrum. The exponent, proportional to Q_B, reflects the contribution of spectral diffusion to the decay of the ESE signal and that proportional to Q_A reflects the contribution of the instantaneous diffusion mechanism. The quantities Q_A and Q_B have been calculated numerically as a function of τ and W_{max} and have been published[29,30].

The experimental decay of the ESE signal in the two-pulse method is associated not only with the dipole–dipole interactions between the electron spins but also with the influence of the nuclei of the matrix and of the spin–lattice relaxation on the phase relaxation of the spins. These mechanisms make a signficant contribution to the decay of the ESE signal amplitude and in practice limit the time interval in which the study is carried out from the "ringing" time of the cavity (~0.3 μs) to τ = 2–3 μs. In this interval, the functions Q_A and Q_B can be represented by linear functions in τ for the rates W_{max} in the $0–10^4$ and $10^3–10^5$ s^{-1} ranges. This makes it possible to represent the decay of ESE signal in a general form for systems with a uniform distribution[6,7,30]:

$$V(2\tau) = V(0)\exp(-2b\tau),$$
$$b = b_0 + \left[\alpha_C + \alpha_M\left\langle \sin^2\frac{\theta}{2}\right\rangle_{g(\omega)}\right]c_{av}, \qquad (2)$$
$$b_0 = m\tau^n + T_{2l}^{-1}, \quad \alpha_M c_{av} = \Delta.$$

where $m\tau^n$ is the term corresponding to the electron–nuclear interaction, n = 1–2 and T_{2l}^{-1} is the rate of phase relaxation due to the spin–lattice interaction. In the limiting case where the coefficient $\alpha_M = 8.2 \times 10^{-13}$ cm^3 s^{-1} the quantity Δ corresponds to the static dipole line width.

Relations of type (2) have been observed in the study of the phase relaxation of a whole series of systems with a uniform distribution of paramagnetic species[6,7]. By studying the dependence of the rate of phase relaxation on the average concentration and θ for a known EPR spectrum, whose form is determine by the type of $g(\omega)$, it is possible to obtain α_C and α_M. As an example, Fig. 3 presents data for the concentration dependence of the rate of phase relaxation for vitreous solutions of VO^{2+} ions in sulphuric acid and for solutions of the stable diphenylpicrylhydrazyl radical in methanol (77 K) and Fig. 4 illustrates the dependence of the rate of phase relaxation on the quantity $\langle\sin^2\theta/2\rangle$ for the $\dot{C}H_2OH$ radicals in methanol γ-irradiated at 77 K. We may note that for absorbed γ-radiation doses in excess of 2000 Gr, these radicals are stabilised uniformly in the matrix[32].

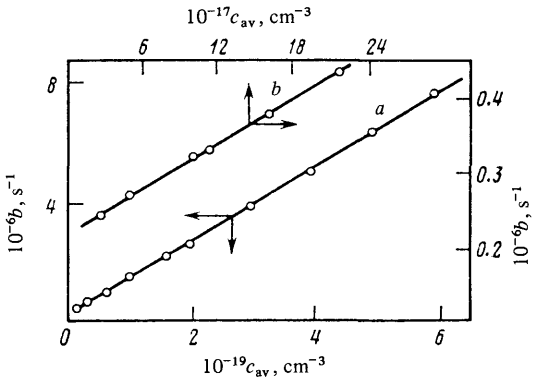


Figure 3. Dependence of the rate of phase relaxation on the concentration of VO^{2+} ions in frozen aqueous sulphuric acid solutions (*a*) and for frozen solutions of diphenylpicrylhydrazyl in methanol (*b*); temperature 77 K.[6,7]

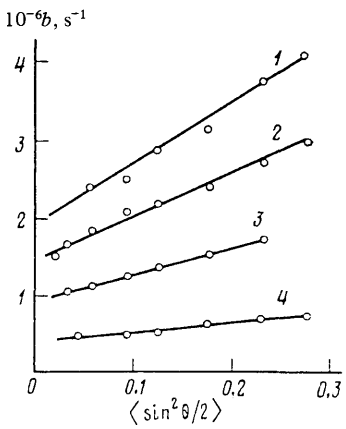


Figure 4. Dependence of the rate of phase relaxation for CH_2OH radicals in methanol (77 K) on the spectrum excitation conditions ($\theta = \gamma H_1 \tau_p$) at different radical concentrations (cm^{-3}): 1) 3×10^{19}; 2) 2.2×10^{19}; 3) 1.3×10^{19}; 4) 0.4×10^{19}. The external magnetic field H_0 is fixed and corresponds to the central line of the triplet in the EPR spectrum of the CH_2OH radical[6,7].

Thus, together with the results of the study of the dependence of the ESE signal amplitude on τ, the investigator obtains a fairly complete set of experimental data characterising the physical mechanism of the phase relaxation in the spin system. The factor important for applications is that the study of phase relaxation leads in its turn also to procedures for the investigation of spatial distribution of paramagnetic centres in solids.

In conformity with the foregoing, the spatial distribution of species determines the rate of decay of the ESE signal in the two-pulse method. As for any inversion problem, it is not possible to obtain directly from the rate $V(2\tau)$ information about the relative spatial distribution of species in the test system, which can be characterised, for example, by the pair distribution function $n(r)$ [$n(r)$ is the probability of finding species at a distance r from one another]. There exist two procedures which facilitate this problem. The first involves the calculation of $V(2\tau)$ for different $n(r)$. A series of interesting results have been obtained recently in this way, but these require a direct experimental test[31]. The second procedure involves modelling the function $n(r)$ investigated by a known function for a uniform distribution of species in a limited isolated volume, which corresponds to the introduction of the concept of a local concentration c_{loc}. If it is assumed that the species are for some reason localised uniformly in a volume $v_{loc} < v_0$, where v_0 is the volume of the specimen, then the decay of the ESE signal can be formulated thus:

$$V(2\tau) = \exp\{-c_{loc} \int d^3r[1 - V_p(2\tau, r)]\}$$

and one can assume subsequently that, in terms of this approximation for systems with a non-uniform distribution of species, relations of type (2) hold, where the quantity $c_{loc} = c_{av}v_0/v_{loc}$ is used as the concentration. Such model concepts concerning the spatial inhomogeneity or the presence of c_{loc} are widely used in the study of radical tracks in irradiated solids.

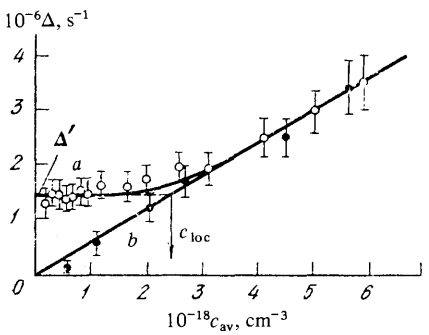


Figure 5. Dependence of the dipole line width Δ on the average concentration of the O^- radical-ions stabilised after the β-irradiation (*a*) and γ-irradiation (*b*) of 9 M aqueous NaOH solutions at 77 K.[33] The local concentration can be obtained from the value of Δ' or from the region of the inflection in the $\Delta(c_{av})$ curve, where $c_{av} = c_{loc}$.

We shall consider briefly only the most significant results obtained recently.

Track effects are manifested most strikingly in the study of the dependence of the relaxation time on the adsorbed dose D or on the average radical concentration in the course of irradiation ($c_{av} = G_R D$, G_R is the radiation yield of the radicals). A typical result for the O^- radical-ions, formed together with the captured electron on β-irradiation of an aqueous 9 M NaOH solution at 77 K, is illustrated by curve *a* in Fig.5.[33] In this system the kinetics of the phase relaxation for the O^- radical-ion are described by Eqns.(2), where $n = 2$, and the main contribution to the rate of phase relaxation comes from the instantaneous diffusion mechanism. The rate of phase relaxation p and the dipole width Δ hardly change at low radical concentrations (before the overlap of the tracks). Subsequently, when the absorbed dose and the overall concentration increase, the dipole interaction between the radicals in different tracks becomes significant. These parameters (*b* and Δ) begin to vary linearly as a function of the average concentration, as for a uniform distribution of radicals or for γ-irradiated specimens (Fig.5, curve *b*), where the track effect can be manifested only for very small absorbed radiation doses.

Track effects had not been observed either in the study (in the course of γ- and β-radiolysis) of the concentration dependence of the rate of relaxation for another particle stabilised in this system, namely the captured electron.

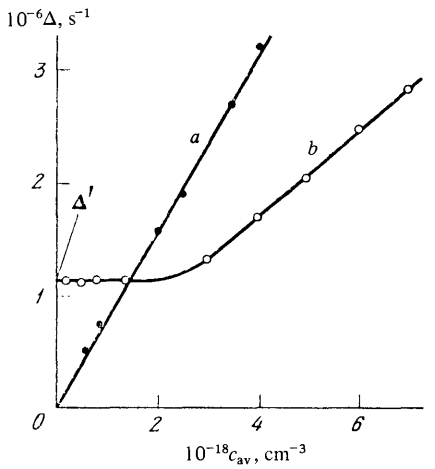


Figure 6. Dependence of the dipole line width on the concentration of paramagnetic species observed on β-irradiation of 1 M solutions of Cd^{2+} ions in methanol at 77 K:[34] *a*) Cd^+ radical-cations; *b*) $\dot{C}H_2OH$ radicals.

IV. RADICAL TRACKS

When the specimen is irradiated, th ionising particle generates positively charged ions and electrons along its path in the solid. As a result of a series of chemical reactions, these primary radiolysis products can be transformed into free radicals or atoms forming a spatially localised track. The appearance of such tracks, particularly for particles with a high ionisation intensity (α- and β-particles, products of nuclear reactions), has been observed and investigated by ESE in studies which have already been reviewed[6,7,12].

Fig.6 presents the results of studies of methanol with added Cd^{2+} ions (0.1–1.0 M), which function as acceptors of the captured electrons. Data for track effects had been obtained earlier for the $\dot{C}H_2OH$ radicals in methanol frozen at 77 K and for its acid solutions[6]. A system with an acceptor proved to be more informative: it was possible to investigate the phase relaxation of both methanol radicals and the Cd^+ radical-cations, because their EPR spectra overlap only partially. A detailed study of the phase relaxation for these species has been carried out[34]. Analysis of the instantaneous diffusion

mechanism yielded the dependence of the dipole line width Δ on the absorbed dose or on the concentration during irradiation (Fig.6).

The local concentrations of the radicals in the track can be determined from the dipole broadening Δ' in the region of track effects or from the concentration of radicals corresponding to the transition region where $c_{av} = c_{loc}$:

$$c_{loc} = \Delta'/\alpha_p \ .$$

The value of α_p can be determined in experiments for the same systems with a uniform distribution of radicals (γ-irradiation). Assuming further that the radical track is an infinitely long cylinder in which the species are distributed unformly, it is possible to determine the radius of such a track:

$$R_{tr} = \left(\frac{G_R \cdot \overline{LET}}{100\pi c_{loc}}\right)^{1/2}$$

where LET is the average linear energy transfer for the given type of radiation.

For a limited volume of any shape, the contribution of the dipole–dipole interaction to the decay of the ESE signal differs from the contribution for an infinitely large specimen even if the species are distributed uniformly within a limited volume. The corrections R_{tr} due to this effect have been calculated[35]. The quantity G_R is determined independently by the stationary EPR method from the average concentrations of radicals for different irradiation doses (radical accumulation curve). Naturally, when the linear dependence on the rate of relaxation or Δ on the concentration is observed over the entire experimental range of doses, then there is a possibility only of estimates of the upper limit to the values of R_{tr}.

The study of phase relaxation makes it possible to determine the local concentration of paramagnetic species in the solid up to 10^{17}–10^{18} cm^{-3}. In certain cases, for example, for hydrogen atoms[36], it is possible to measure concentrations up to 10^{16} cm^{-3} if the method of consecutive series is used, in which the kinetics of the recovery of the ESE signal are investigated as a function of the repetition frequency of a series of UHF pulses. The kinetics of the restoration of the ESE signal are in this case determined by the spin–lattice relaxation and the spin diffusion; the latter depends also on the intensity of the dipole–dipole interaction between the paramagnetic species, which leads to possibilities for estimating c_{loc}.

The kinetics of the spin–lattice relaxation as a function of the concentration of the paramagnetic species in α- and β-irradiated 8 M solutions of sulphuric acid have been investigated[36] at 77 K. The same local concentrations of hydrogen atoms (10^{18} cm^{-3}) were found for the α-tracks as in the study of the phase relaxation in the given system[37]. In contrast to the earlier investigation[37], for β-irradiation it was possible to obtain a more accurate estimate of the local concentrations: $[\dot{H}]_{loc} = 1^{+1.0}_{-0.5} \times 10^{16}$ cm^{-3}.

Thus data have now been obtained about the radical tracks in alkaline, acid, and alcoholic glasses. The mechanism of the radiolysis in these systems has been investigated fairly thoroughly and includes mainly ionic and radical stages leading to the stabilisation of radicals of two types at low temperatures—formed as a result of the reactions of secondary electrons [$\dot{R}(-)$] and those formed by the reactions of positive ions [$\dot{R}(+)$].

In alkaline glasses the precursor of the captured electron e_t is a secondary electron e^- and the precursor of the O^- radical-ion is the H_2O^+ ion[38]:

$$H_2O \rightsquigarrow H_2O^+ + e^- ,$$
$$e^- \rightarrow e_t^- ,$$
$$H_2O^+ + H_2O \rightarrow H_2O + H_2O^+ ,$$
$$H_2O^+ + OH^- \rightarrow H_2O + \dot{O}H ,$$
$$\dot{O}H \rightarrow H^+ + O^- \ .$$

In acid glasses the main radical formation processes can be represented schematically as follows[39]:

$$SO_4^{2-}, (H_2O) \rightsquigarrow SO_4^-, (H_2O^+) + e^- ,$$
$$e^- \rightarrow e_t^- ,$$
$$e_t^- + H^+ \rightarrow \dot{H} ,$$
$$H_2O^+ + SO_4^{2-} \rightarrow H_2O + SO_4^- .$$

In this case the precursor of the $\dot{H}$ atom is a secondary electron and the precursor of the SO_4^- radical-anions is the ionised state of water or SO_4^{2-}. For methanol solutions with Cd^{2+}, the precursors of radical species can also be readily identified, because the main processes are described by the following scheme:

$$CH_3OH \rightsquigarrow CH_3OH^+ + e^- ,$$
$$e^- \rightarrow e_t^- ,$$
$$e_t^- + Cd^{2+} \rightarrow Cd^+ ,$$
$$CH_3OH^+ + CH_3OH \rightarrow CH_3OH_2^+ + \dot{C}H_2OH \ .$$

In the system indicated, it is possible to use the ESE method to investigate the spatial distribution of radicals of two types: $\dot{R}(+)$ and $\dot{R}(-)$. Data for γ-irradiation are compiled in the Table, which reveals the following features: (1) the tracks for the radicals $\dot{R}(+)$, whose precursors are positive ions, have radii of 30–50 Å and are characterised by a local radical concentration of 10^{18}–10^{19} cm^{-3}; (2) if the precursor of the radical is a secondary electron, then the size of the radical track increases to values exceeding 100 Å or more and the local concentration corresponding to doses greater than 5×10^3 Gr is equal to the average concentration; (3) the radiation yields $G_{\dot{R}(+)}$ and $G_{\dot{R}(-)}$ in the systems investigated are almost equal.

The radiation yields of the radicals, their local concentrations, and dimensions of the tracks for certain β-irradiated polar solutions frozen at 77 K.[33–37]

Solution	$\dot{R}(+)$	$\dot{R}(-)$	G_R (for 100 eV)	$10^{-16} c_{loc}$, cm^{-3}	R_{tr}, Å
8 M H_2SO_4	SO_4^-	—	1.5	600	30
8 M H_2SO_4	—	$\dot{H}$	1.5	1	400
9 M NaOH	O^-	—	2.6	400	50
9 M NaOH	—	e_t^-	2.7	20	160
1 M Cd^{2+} in CH_3OH	$\dot{C}H_2OH$	—	2.5	1000	25
1 M Cd^{2+} in CH_3OH	—	Cd^+	2.5	30	130

These data can be accounted for by a detailed analysis of the elementary stages involving the formation, transport, and stabilisation of the radical radiolysis products in the

systems investigated. The radius of the radical track of the $\dot{R}(+)$ species is determined both by the size of the ionisation region and by the positive charge migration reactions. The spatial distribution of the species $\dot{R}(-)$ is determined by the path traversed by secondary electrons before their thermalisation and capture by a trap or an acceptor and by the reverse recombination reaction. A detailed discussion of these problems is outside the scope of this review; it can be found in other publications[34,40-42]. We shall only mention that the results obtained by the ESE method can be regarded as direct confirmation of the model ideas concerning the spatial distribution of radicals in the track of a charged particle, which were put forward as early as the 1950s by Lea[43], Gray[44], and Frolich and Platzman[45].

Studies have also been made on methanol with a Cd^{2+} acceptor on irradiation with species having higher values of LET than for β-particles[40]. Two interesting results were obtained. Firstly, a wide range of absorbed doses was observed in which the rate of phase relaxation is independent of the dose, namely up to concentrations $[\dot{C}H_2OH] \simeq 1.5 \times 10^{19}$ cm^{-3}, which indicates higher values of c_{loc} for these systems. Secondly, it was found that only 10–20% of the $\dot{C}H_2OH$ radicals are involved in the generation of the ESE signal, while the remaining species have phase relaxation times $T_2 < T_{2,min}$ (in the experiments considered $T_{2,min} =$ 400 ns) and do not contribute to the amplitude of the ESE signal. Evidently the local concentration of radicals with short T_2 is greater than 10^{19} cm^{-3}. It has been suggested that they are stabilised in the central part of the track.

An important confirmation that such radical stabilisation is inhomogeneous with respect to the radius of the track has been provided by experiments on photoannealing in such systems. Under the influence of ultraviolet light, the Cd^+ radical-cations interact with methanol, which results in the formation of $\dot{C}H_2OH$ radicals which have a random, uniform spatial distribution in the matrix as a consequence of a series of photochemical reactions and diffusion. Fig.7 illustrates the variation of the amplitude of the ESE signal for the $\dot{C}H_2OH$ radicals during photoannealing. Partial recombination leads to some decrease of the radical concentration determined by the stationary EPR method. On the other hand, the intensity of the ESE signal increases by a factor of six. The diffusion of radicals from the dense part of the track increases their phase relaxation time, which leads in its turn to an increase of the intensity of the ESE signal.

The experiments described show that the radical track has a complex three-dimensional structure and the hypothesis that they consist of cylinders with a uniform distribution of paramagnetic species can be adopted for the interpretation of experimental data only as a first approximation.

In the general case the local concentration constitutes an average characteristic of the spatial distribution of the species. The interpretation of its changes in the course of chemical reactions has not gone beyond qualitative conclusions, which nevertheless proved extremely useful for the understanding of the mechanisms of reactions in solid matrices. It has been shown recently that more detailed information about the relative spatial distribution of species can be obtained by the relaxation probe method and double electron–electron resonance in ESE spectroscopy.

V. THE RELAXATION PROBE. INVESTIGATION OF THE DISTRIBUTION WITH RESPECT TO DISTANCES IN RADICAL–ION PAIRS

Under the influence of light and radiation, paramagnetic species are frequently formed and stabilised as pairs in solids. Different pairs arise both from decomposition of the excited state M* and from ionisation. For example, if the electron is stabilised in the solid phase, the photoionisation of the Ion M^{n+} can give rise to the pairs $M^{(n+1)+}...e_t^-$. The form of the distribution function for such pairs with respect to distance is determined by the lengths of the paths traversed by the electrons, the rates of the reverse electron–ion recombination reaction and the reactions involving electrons and generating atoms or radicals, the diffusion of the latter to their stabilisation sites, and other experimental conditions, i.e. in the general case by the same factors as the geometry of the radical tracks.

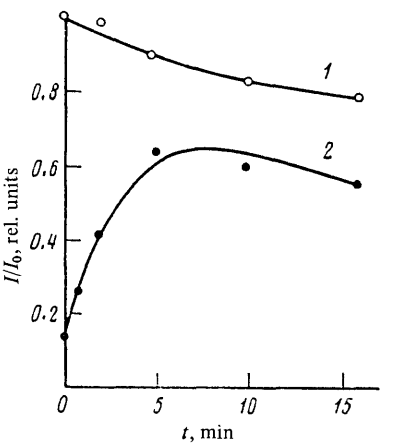


Figure 7. Variation of the relative amplitude I/I_0 of EPR (curve 1) and ESE (curve 2) signals for the $\dot{C}H_2OH$ radicals during photoannealing at 77 K. Specimen—methanol irradiated with α-particles and the ^{7}Li recoil nuclei generated in the reaction $^{10}B(n, \alpha)^7Li$;[40] t = annealing time.

It has been shown in a series of studies[46-51] that the ESE method makes it possible to determine $n(r)$ or to study the properties of this distribution in the case where one of the components of the pair is a species, usually a paramagnetic ion, with a short spin–lattice relaxation time: $T_1 \ll \tau \simeq 10^{-6}$ s.

The main idea of the experiment can be illustrated in the following manner. Radical pairs can be roughly divided into two types. In the pairs of the first type the radicals are close to the ion, within a "black sphere". Owing to the magnetic dipole–dipole interaction with the ion, these radicals have short phase relaxation time T_2^S and make a very small contribution to the intensity of the ESE signal. The main contribution comes from the radicals at large distances from the ion, outside the "black sphere", and having a long relaxation time T_2^l (Fig.8a). The volume of the "black sphere" is defined by the relation

$$V_B = {}^4/_3\pi R^3 \simeq {}^4/_3\pi \left[\frac{2}{3}\gamma^4\hbar^2 S(S+1)\tau_0 T_1\right]^{1/4} \qquad (3)$$

where τ_0 is the time interval between the first and second pulses, which is fixed and is chosen to be the smallest possible, and S is the spin of the ion. Since the relaxation time of the ion T_1 depends on temperature, the radius of the "black sphere" is also a function of temperature and τ_0. The ESE signal intensity depends on the form of the pair distribution function $n(r)$. This dependence is illustrated in Fig.8c which shows how the ESE signal intensity varies with

temperature or with the distance from the ion to the radical in two cases—for the uniform $[n^1(r)]$ and non-uniform $[n_2(r)]$ distributions of the pairs with respect to the distances r. In these experiments the paramagnetic ion behaves as the "probe" of the pair distribution: by altering the temperature and following the signal intensity for the known temperature variation of T_1, it is possible to determine $n(r)$.

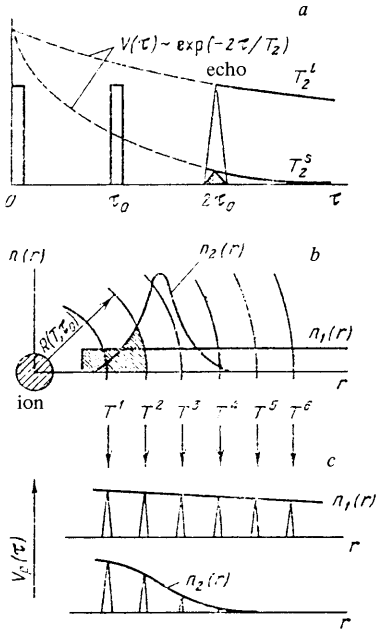


Figure 8. Scheme illustrating the method for the determination of the distribution function with respect to distances in ion–radical pairs from ESE data: *a*) two types of ESE signals arising for a fixed τ from radicals close to the ion (low values of $T_2 = T_2^S$) and remote from the ion (high values of $T_2 = T_2^l$); *b*) schematic representation of the pair distribution function for uniform $[n_1(r)]$ and non-uniform $[n_2(r)]$ distributions; R = radius of the "black sphere" which is different for different temperatures T^i; *c*) dependence of the ESE signal intensity on temperature or distance for two types of $n(r)$.

A theory and methods for the interpretation of the experimental results, which permit the determination of $n(r)$ by the relaxation probe method, have been developed[47,48]. According to the analysis carried out, the function $n(r)$ is given approximately by the relation

$$n(r) = -\frac{d}{dV_B}\left[\frac{V_p(2\tau)}{V_p(0)}\right], \qquad (4)$$

where $V_p(2\tau)$ is the intensity of the ESE signal of the radical in pairs with the ion at a given temperature and for time intervals $\tau = \tau_0$ between the UHF pulses. The quantity V_B, which has the dimensions of volume, is determined experimentally for the same values of the parameters from the relation

$$V_B = -\frac{1}{c_{av}} \ln\left[\frac{V(2\tau)}{V(0)}\right],$$

where $V(2\tau)$ is the spin echo signal intensity for a uniform distribution of the same ions and radicals relative to one another and c_{av} is the average concentration of ions. The distance r is calculated from Eqn.(3).

Thus the experiment reduces to the measurement of the relative intensity of the ESE signal for a fixed τ_0 and different temperatures (1), the measurement of the same quantity for the same system with a uniform distribution of spins (2), and the study of the temperature dependence of T_1 for the ion and V_B(3). The function $n(r)$ is determined by differentiating the experimental curve in accordance with Eqn.(4). The relative accuracy of this method of determination of $n(r)$ is estimated as being to within 30% and the resolving power with respect to r is ~1 Å.[46–48] The relaxation probe method has found applications in studies of the steric characteristics of the formation, diffusion, and reactions of the radicals formed on photolysis and radiolysis of matrices.

1. Distribution of Radicals in Photolysis and Radiolysis

The most detailed information about the function $n(r)$ can be obtained for ions with a fairly short relaxation time $T_1 \ll 10^6$ s. Such ions include Fe^{2+}. A detailed study has therefore been made[47,48] of the pair distribution of the species arising on photolysis of the Fe^{3+} ion in vitreous alcohol matrices via the overall reaction

$$Fe^{3+} + R_2CH(OH) \xrightarrow{h\nu} Fe^{2+} + R_2\dot{C}OH + H^+,$$

where R = H for methanol and R = CH_3 for isopropyl alcohol.

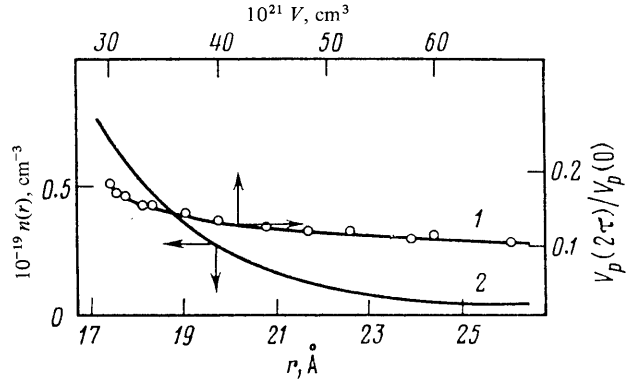


Figure 9. Dependence of the relative ESE signal amplitude $V_p(2\tau)/V_p(0)$ on the volume V_B (curve *1*) and the corresponding pair distribution function (curve *2*) for the Fe^{2+}... $\dot{C}H_2OH$ pairs in methanol irradiated with ultraviolet light[47].

Specimens of two types were investigated—with a spatial distribution of species in pairs (photolysis on irradiation with light at $\lambda > 330$ nm) and with a uniform distribution of radicals. The latter were obtained by photolysis with the unfiltered light of a DRSh-500 lamp, which led to the decomposition of the alcohol radicals into lighter species (for example, CH_3 and HCO in the case of methanol), their diffusion, and their secondary reactions with the matrix. Data were obtained for the dependence of the relative ESE signal amplitude $V_p(2\tau)/V_p(0)$ on temperature and the volume V_B of the "black sphere" (Fig.9, curve *1*). Eqn.(4) makes it

possible to determine the distribution function with respect to radical–ion distances in these experiments (Fig.9, curve 2). For methanol, the function $n(r)$ was found in the range of values of r from 17 to 26 Å; in this range it decreases exponentially with a characteristic descent parameter of 3 Å. Analogous results were obtained also for solutions of Fe^{3+} in isopropyl alcohol.

The analytical form of the functions $n(r)$ in the experiments described cannot be determined for Fe^{2+} ions in the range $r < 17$ Å. The resolving power of the method in the region of short distances (r_{min}) is determined by the possible experimental values of τ_0 and T_1. For $\tau_0 = 0.3 \times 10^{-6}$ s and $T_1 = 10^{-11}$–10^{-10} s, Eqn.(3) yields r_{min} 10–15 Å for ferrous ions. The upper limit, corresponding to $T_1 \cong \tau_0$, is then $r_{max} \cong 70$–100 Å. For the most interesting range $r < 17$ Å, there is, however, a possibility of another approach to the experimental estimation of the form of the function $n(r)$.

If the spin–lattice relaxation time of the ion T_1 is known, it is possible to estimate the relative number of radicals in the region of rapid relaxation (for $r < r_{min}$) by studying the changes in the ESE signal intensity on transition from a non-uniform spatial situation involving pairs to a uniform situation. This can be readily achieved by annealing the specimen at temperatures such that the radical–ion pairs begin to move apart without a significant contribution of recombination. Only an increase of the ESE signal intensity with increase of temperature is observed in such experiments. The constancy of the overall concentration of radicals N_0 is monitored simultaneously by the stationary EPR method. By varying T_1 or τ_0, i.e. the radius of the "black sphere", one obtains a histogram of the spatial distribution—the quantity $\Delta N(r)/N_0$. According to these experiments[47,48], 80% of the total number of Fe^{2+}... $R_2C(OH)$ pairs are located in the range $r < 17$ Å in methanol and isopropyl alcohol (Fig.10*a*).

Analysis of the mechanism of the formation of radicals in frozen solutions in alcohols containing Fe^{3+} ions[52,53] showed that, when light is absorbed by the ion introduced into the alcohol in the form of a halogen complex, phototransfer of an electron from a matrix molecule to the complex takes place. Such phototransfer is apparently most likely for the alcohol molecules closest to the complex. The data obtained by the ESE method (Fog.10*a*) concerning the mutual spatial distribution of ions and radicals are therefore consistent with the hypothesis of the phototransfer of an electron from the matrix. However, since the characteristic average distance in the ion–radical pairs is ~12 Å, one must assume that the radicals are not stabilised at the site of their formation in the first coordination sphere of the complex but execute several jumps up to the stabilisation site. This also gives rise to a set of distances characterising the function $n(r)$, which describes the "tail" of the distribution (Fig.9).

The pair distribution of the species formed on photolysis of M^{n+} ions (where $M^{n+} = Fe^{2+}$ or Cr^{2+}) in glasses of an aqueous solution of sulphuric acid has been investigated by the ESE method[46,49]:

$$M^{n+}(H_2O) \xrightarrow{h\nu} M^{(n+1)+} + \dot{H} .$$

The relaxation time T_1 for these ions is ~10^{-7} s and does not differ significantly from the limiting value $\tau_0 \cong 10^{-6}$ s. It is therefore not possible to determine the detailed form of the function $n(r)$. It has been found by the method involving the isothermal annealing of the specimen that ~80% of the atoms are located at distances from the ion up to 50 Å.

A change in the line shape of the H and D atoms has been observed[49] in the stationary EPR spectrum during annealing. This effect has also been attributed to the characteristic pair distribution of species in the system investigated. Its analysis makes it possible to refine significantly the distribution of the pairs: approximately 30% of the total number of pairs should have distances from 0 to 17 Å. The histogram which follows from the ESE and EPR data on the system indicated is illustrated in Fig.10*b*.

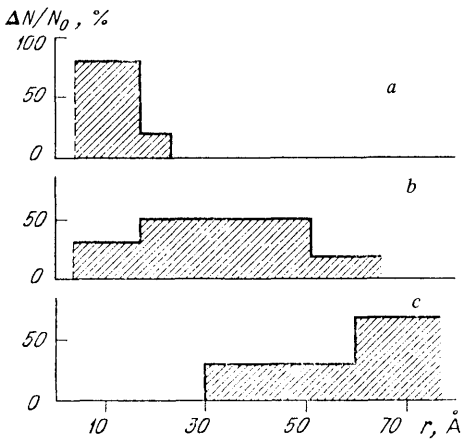


Figure 10. Histograms of the distribution with respect to the distances r in the radical–ion pairs formed on photolysis (*a* and *b*) and radiolysis (*c*) of polar frozen solutions (according to the data in Refs.46–49): *a* Fe^{3+} + RHOH $\xrightarrow{h\nu}$ Fe^{2+}... ROH (R = CH_2, $(CH_3)_2C$); *b* M^{2+} + H_2SO_4 $\xrightarrow{h\nu}$ M^{3+}...H (M = Fe, Cr); *c* $D_2SO_4 \xrightarrow{\gamma} \dot{D}$... SO_4^-.

Two alternative mechanisms for this photochemical reaction have been discussed[54]. According to one of them, the primary reaction step is electron transfer to the water molecule closest to the ion. After this, the H_2O^- species either decomposes into H and OH^- or reacts with H_3O^+ to form H. In the second mechanism, a mobile electron is formed under the influence of light, diffuses through the matrix, and reacts with the acceptor. Recently published experimental data[54,55] support the first mechanism.

If the mobile electron is not formed in the primary step (i.e. the first mechanism is valid), the experimental spatial distribution of H atoms relative to the Fe^{2+} and Cr^{2+} ions implies that the atoms are not stabilised at the site of their formation and diffuse until they are captured by a trap. The distribution function for the pairs with respect to distances has the following form for a model of this kind[56]:

$$n(r) = [4\pi r_0^2 r]^{-1} \cdot \exp[-r/r_0] .$$

It was found that the function describes equally well data obtained by the ESE method and EPR with $r_0 = 15$ Å.

The distribution $n(r)$ for the pairs SO_4^-... H(D), formed on γ-radiolysis of an aqueous solution of sulphuric acid, has been investigated[50]. In this case the mechanism of the formation of the pairs is associated with the ionisation of SO_4^{2-} and H_2O (D_2O) and the capture of a secondary electron by the $H^+(D^+)$ ion. In the determination of $n(r)$ in an analytical form, the same difficulties arise as for the ions Fe^{3+} and Cr^{3+}, since $T_1 = 10^{-6}$ s for SO_4^-. Analysis of the kinetics of the decrease of the ESE signal for the $\dot{D}$... SO_4^- pairs showed that the fraction of pairs with distances from 0 to 60 Å is ~30%. On the basis of considerations concerning the

possible lengths of the paths traversed by a secondary electron, the function describing the distribution of secondary electrons with respect to distances[41], as well as data for the experimental yield of pairs, it has been concluded[50] that a region $0 < r < 30$ Å with zero values of $n(r)$ exists as a result of primary recombination in the spatial distribution of pairs. The histogram for this case is illustrated in Fig.10c.

Thus the series of experiments carried out by the ESE method made it possible to obtain for the first time direct information about the spatial pair distribution of the paramagnetic species formed on ultraviolet and γ-irradiation of a series of polar substances.

2. Diffusion of Radicals

As a result of diffusion, the paramagnetic centres gradually emerge from the "black sphere" near the ion and their phase relaxation times increase, which leads to an increase of the ESE signal intensity for a fixed τ_0. Ultimately, the ESE signal intensity reaches a constant value at long times which corresponds to a uniform distribution of radicals in the system.

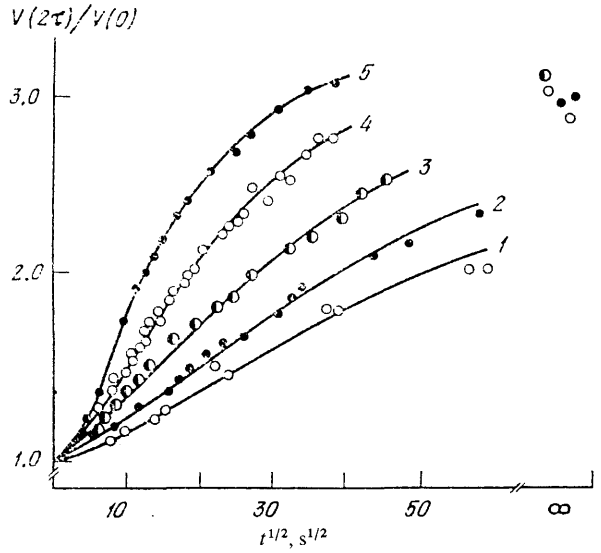


Figure 11. Increase of the ESE signal intensity during the annealing at different temperatures of specimens with $Fe^{3+}...H$ pairs arising on photolysis of Fe^{2+} solutions in 7 M H_2SO_4;[46] temperature (K): 1) 90.1; 2) 91.3; 3) 93; 4) 95; 5) 97.

The dependence of the ESE signal intensity on the annealing time at different temperatures has been investigated[46] for the $Fe^{3+}...\dot{H}$ pairs formed on photolysis of Fe^{2+} ions in frozen solutions of sulphuric acid (Fig.11). The degree of enhancement of the echo signal amplitude on diffusion is determined by the product of the diffusion coefficient of hydrogen atoms and the characteristic annealing time, for example the time of attainment of half the limiting intensity of the ESE signal ($t_{1/2}$) at a given temperature. When the Arrhenius temperature dependence obtains, we have

$$t_{1/2} = D_0^{-1} \exp(E/RT) .$$

$E = 5.5 \pm 0.5$ kcal mol^{-1} and $D_0 = 7 \times 10^{-4}$ cm^2 s^{-1} were found for H atoms from measurements of $t_{1/2}$ at different temperatures in the range 90–100 K.

More detailed information about the mechanism of diffusion in a solid can be obtained by studying the changes in the pair distribution function at different times during diffusion. Such studies have been carried out for radicals in alcohol glasses containing the $Fe^{2+}...R_2\dot{C}OH$ pairs for methanol and isopropyl alcohol[47]. With increased annealing time, the $n(r)$ distribution density tends to zero, as is to be expected from the diffusion equation. This has in fact been observed, for the $Fe^{2+}...\dot{H}$ pairs[46]. In studies of the diffusion of radical–ion pairs in alcohols, it was, however, found that the spatial scale of the diffusion is limited. Starting from a certain instant at a constant annealing temperature, the form of the pair distribution function virtually ceases to depend on the annealing time. This is illustrated by the results of the experimental determination of the pair distribution function with respect to distances at different times, presented in Fig.12*a* for radicals in methanol. For example, at an annealing temperature of 96.5 K, the principal changes in the function $n(r)$ take place during the first two minutes of annealing, which follows from a comparison of curves *0* and *1*. A further increase of annealing time at 96.5 K by an order of magnitude does not entail significant changes in $n(r)$ (curve *2*). An analogous pattern can be observed also in the group of curves characterising the variation of $n(r)$ during annealing at 100 K (curves *3*–*5*). Only an increase of temperature to 112 K results in $n(r)$ close to zero.

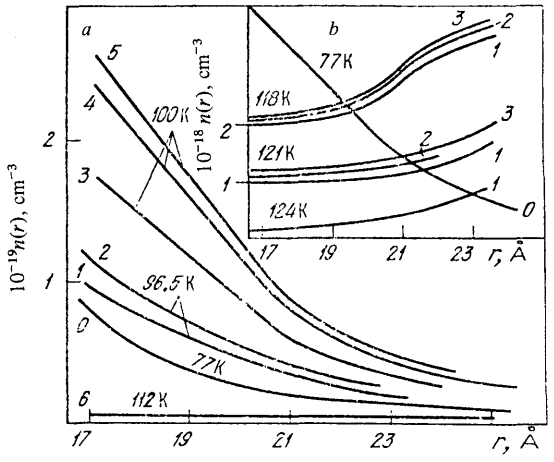


Figure 12. Variation in the course of thermal annealing of the pair distribution function for radical–ion pairs: *a*) $Fe^{2+}...\dot{C}H_2OH$ pairs in methanol; 0) initial $n(r)$ at 77 K; 1) and 2) annealing at 96.5 K for 2 and 20 min respectively; 3)–5) annealing at 100 K for 4, 9, and 19 min respectively; annealing at 112 K for 1 min; *b*) $Fe^{2+}...(CH_3)_2\dot{C}OH$ pairs in isopropyl alcohol; 0) initial $n(r)$. In each group of annealing curves at 118, 121, and 124 K the annealing times are 1, 2, and 6 min for curves *1*, *2*, and *3* respectively.

An analogous picture has been observed for radicals in isopropyl alcohol (Fig.12*b*). The difference from methanol consists only in the fact that, in addition to diffusion, raising the temperature results in a reaction between the radicals

and the ion in which a radical-ion complex is formed. Ultimately the distribution function $n(r)$, established as a result of diffusion and the reaction, does not have a descending form as in the case of methanol but actually increases with increase of r. In the vicinity of the ion a minimum in the distribution density is observed. We may note that the formation of a hydrogen atom–ion complex had been observed earlier for other systems—for iron[57] and copper[58] ions.

The observed characteristics of the diffusion of radicals have been interpreted[47] taking into account the fact that in glasses there are distributions with respect to intermolecular distances, mobilities, and other parameters between different sites. As a consequence of the distribution with respect to diffusion parameters, the radical probably diffuses only as far as the cell which it finds difficult to leave at the given temperature and is trapped there. The higher the temperature the longer the path which it traverses in the search for a suitable trap and the initial pair distribution becomes more diffuse. We may note that analogous characteristics are known for the kinetics of the recombination of radicals in solids: the kinetic curves frequently tend to a limit or have a "stepped" form with a rapid variation of the concentration in the region of short chemical reaction times and a slow change in the region of long chemical reaction times (see, for example, Blyumenfel'd et al.[59]).

3. Changes in the Pair Distribution During Chemical Reactions of Radicals

By studying the pair distribution function in the course of chemical reactions in the matrix by the relaxation probe method, it is possible to infer the scale of the migration of the valence in various elementary steps. Such studies have been carried out for radicals formed on photolysis of Fe^{3+} solutions in isopropyl alcohol[51]. In this system, there is a possibility of various chemical reactions induced by light or by heating the specimen.

Irradiation with light at $\lambda > 330$ nm leads to the formation of pairs consisting of the alcohol radicals $(CH_3)_2\dot{C}OH$ and Fe^{2+} ions. The pair distribution function $n(r)$ in the above reaction has been studied in detail for the range of distances 17–23 Å (as for methanol); the results are presented in Fig.13 (curves *a*). On illumination with light at $\lambda > 300$ nm, the radicals $(CH_3)_2\dot{C}OH$ are transformed into isopropyl radicals $(CH_3)_2\dot{C}H$ by the reaction

$$(CH_3)_2\dot{C}OH + (CH_3)_2CH(OH) \xrightarrow{h\nu} (CH_3)_2\dot{C}H + H_2O + (CH_3)_2CO \quad (5)$$

The concentration of the radicals and the changes in their structure are monitored simultaneously using stationary EPR spectra. After the complete conversion of the alcohol radicals into alkyl radicals, a study was made of the function $n(r)$ for these radicals (Fig.13*b*).

A further three types of reaction can be carried out for the same system on heating or illumination of the specimen and the pair distribution function can be investigated after these transformations. When a specimen containing propyl radicals is heated at 106 K, the substitution reaction

$$(CH_3)_2\dot{C}H + (CH_3)_2CH(OH) \xrightarrow{106\,K} (CH_3)_2\dot{C}OH + (CH_3)_2CH_2 \quad (6)$$

regenerates the alcohol radicals whose pair distribution function is illustrated in Fig.13 (curves *c*). The isopropyl radicals obtained via reaction (5) isomerise under the influence of light at $\lambda > 250$ nm:

$$(CH_3)_2\dot{C}H \xrightarrow{h\nu} CH_3CH_2\dot{C}H_2 \quad (7)$$

In reaction (7) the function $n(r)$ hardly changes and remains close to curve *b* in Fig.13. On the other hand, the propyl alcohol generated by reaction (7) interacts with the matrix at 106 K, regenerating the alcohol radicals:

$$CH_3CH_2\dot{C}H_2 + (CH_3)_2CH(OH) \xrightarrow{106\,K} CH_3CH_2CH_3 + (CH_3)_2\dot{C}OH \quad (8)$$

For the latter, the distribution function proved to be constant and corresponds to a uniform distribution of species.

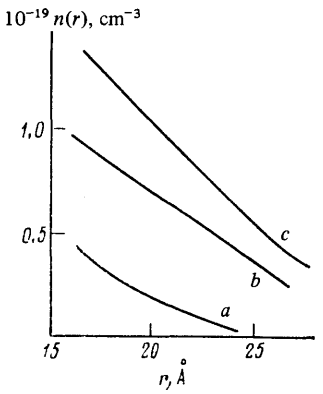


Figure 13. Variation of the form of the pair distribution function $n(r)$ due to chemical reactions in frozen Fe^{3+} solutions in isopropyl alcohol[51]: *a*) initial function $n(r)$ for the $Fe^{2+}...(CH_3)_2\dot{C}OH$ pairs; *b*) the $n(r)$ distribution function for the $Fe^{2+}...(CH_3)_2\dot{C}H$ pairs formed via reaction (5) (see text); this function does not change in reaction (7); *c*) the $n(r)$ function for the $Fe^{2+}...(CH_3)_2\dot{C}OH$ pairs formed in reaction (6).

The spatial migration of the valence for the corresponding reaction can be inferred from the distances between points with identical values of $n(r)$ on the curves in Fig.13. The lattice parameter of isopropyl alcohol is ~4.6 Å. The results presented show that reaction (6) takes place within a "cage" (the valence migrates over a distance of 3–4 Å); in reaction (5) the isopropyl radical is not stabilised at the site of its formation but executes 1–2 jumps before it is captured by a suitable trap (the displacement is by ~8 Å). The propyl radical diffuses over appreciably longer distances (≳20–30 Å) in the course of reaction (8) in the matrix. Within the limits of the accuracy of the measurements, the isomerisation reaction (7) leads to the migration of the valence over distances ≲1 Å.

VI. THE DOUBLE ELECTRON–ELECTRON RESONANCE METHOD IN ESE SPECTROSCOPY AND ITS APPLICATIONS

The spin probe method is applicable for fairly short T_1 of one member of the pair of spins. If the spins *A* and *B* in the pair have similar and fairly long relaxation times T_1, then phase relaxation can be used in the analysis of their spatial distribution, as in the study of radical tracks. However, this is possible only when the difference between the Zeeman frequencies $\omega_A - \omega_B < \gamma H_1$, i.e. under the conditions of the excitation of the complete EPR spectrum.

A method has been proposed[60] for the investigation of the pair distribution of species with similar or even equal T_1 and different ω_A and ω_B. The method is based on the observation of the variation of the ESE signal amplitude for the spins A when the UHF pumping pulse is switched on at a frequency ω_B (Fig.14). Such an influence on the spins B alters the local field at the site of the location of the spin A, by an amount whose magnitude is determined by the dipole–dipole interaction between A and B. Additional dephasing of the precession of the spins A arises, which reduces in its turn the echo signal amplitude A_A due to A compared with its value V_A^0 in the absence of the pulsed pumping of the spins B; thus the UHF pulse at a frequency ω_B stimulates the instantaneous diffusion process. An analogous formulation of the experiment can be found also in NMR spectroscopy[61].

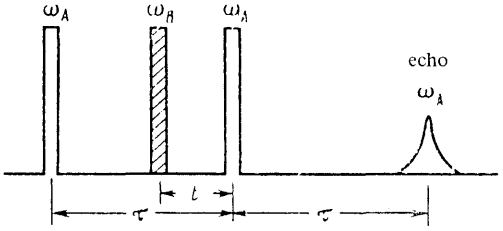


Figure 14. The sequence of the effects of the UHF pulses and the pumping pulse generating the ESE signal in the pulsed double electron–electron resonance method.

A theory of the method has been developed[60] and it has been shown that the experimental ratio V_A/V_A^0, measured for different concentrations of the pairs and extrapolated to zero concentrations of spins (in order to eliminate the decay of the signal owing to the dipole interaction between the pairs), is related to the pair distribution function $n(r)$ by the integral equation

$$[V_A/V_A^0]_{c\to 0} = 1 - p\left[1 - \int_0^\infty 2\pi r^2 n(r) K(u)\, dr\right] \qquad (9)$$

where $p = \langle \sin^2 \theta_B/2 \rangle_{g(\omega B)}$ is the fraction of the spins B excited by a pulse at a frequency ω_B and the averaging is carried out with respect to the EPR spectrum of the species B; $K(u)$ is a function determined by the dipole interactions of the spins of A and B:

$$K(u) = \frac{1}{2}\int_0^\pi \cos[u(1 - 3\cos^2\theta)] \sin\theta d\theta ,$$

where $u = \gamma^2 h r^{-3} t$, θ is the angle between H_0 and the vector $\mathbf{r}$ connecting A and B and t is the time interval between the pulse at a frequency ω_B and a second pulse at a frequency ω_A.

As an example, a study has been made[60] of pairs consisting of hydrogen atoms and the parent hydroquinone radicals formed on photolysis at 77 K of vitreous solutions of hydroquinone in 8 M sulphuric acid solutions. A bimodal cavity of the type already described[62], was used in the ESE spectrometer for such experiments. The specimen was placed at the antinode of the magnetic field for both modes, one of which tuned to the frequency ω_A (hydrogen atoms) and the other to ω_B (hydroquinone radicals). The variation of V_A/V_A^0 was investigated for different times t and radical concentrations c_B. Identical results were obtained for the Ḣ and Ḋ atoms.

In the analysis of the experimental data, an approximate calculation of the values of $n(r)$ by Eqn.(9), in which the core $K(u)$ was replaced by a stepped function, was carried out. In this case, graphical differentiation of the experimental curve represented by the expression

$$V(t) = 1 - [1 - (V_A/V_A^0)_{c_B\to 0}]\frac{1}{p}$$

with respect to the parameter $r = (0.83\gamma^2 ht)^{1/3}$ yields the required distribution function in the form $2\pi r^2 n(r)$. The graph of this function, having a maximum at $r \cong 45$ Å, is presented in Fig.15. Its integration shows that 63% of the pairs are contained in the range 0–85 Å. The remaining pairs have $r > 85$–100 Å and the character of their distribution cannot be determined, since they make a small contribution to the $V(t)$ relation.

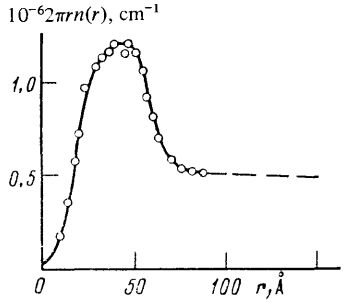


Figure 15. The distribution function with respect to distances for the Ḣ atom–hydroquinone radical pairs formed on photolysis of hydroquinone solutions in 8 M sulphuric acid frozen at 77 K.[60]

According to Shelimov et al.[63] and Bazhin[64], the paramagnetic species in the above system are formed as a result of the photoionisation of hydroquinone (ArH):

$$ArH + H_2O(H_3O^+) \xrightarrow{h\nu} (ArH^+) + \dot{H} + OH^-(H_2O) .$$

The observed distribution of pairs with respect to distances can therefore be due to two processes: the migration of electrons until their capture by a hydronium ion and the diffusion of hydrogen atoms until their stabilisation in traps. Estimates have shown that the energy of the secondary electron arising on photoionisation of hydroquinone in this system does not exceed 1 eV. For electron energies in the range 1–2 eV, the distances traversed in water are 25 Å.[41] On the other hand, according to the results described above[49], the average diffusion distance to the trap is 30 Å. The maximum of the distribution function for the pairs (ArH^+)...H at $r \cong 45$ Å corresponds to the overall contribution of both processes. Further studies are necessary to elucidate the role of different transport processes in the establishment of an inhomogeneous pair distribution in reactions whose primary stage is photoionisation.

By virtue of its greater universality compared with the relaxation probe method, it is to be expected that the double electron–electron resonance pulse method will find extensive application in the future in studies of the spatial distribution of species.

The results discussed above show that ESE constitutes a direct and informative method for the investigation of the spatial distribution of paramagnetic species in the solid

phase. With the aid of ESE, there is a possibility of both a qualitative approach, yielding information about the possible local radical concentrations, and of studies of characteristics such as the pair distribution function of paramagnetic species and the changes in the latter during diffusion and chemical reactions in a solid.

The physicochemical applications of the ESE method, one of which was examined in the present review, are based on the physical theory of the method, which has been fairly adequately developed at the present time, and a continually improving experimental base. It is to be expected that in the future ESE will occupy among the applications of microwave spectroscopic methods in chemistry a place no less important than that of the stationary EPR spectroscopy.

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Unsaturated Adamantane Derivatives

E.I.Bagrii and A.T.Saginaev

The literature data on the methods of synthesis and the physical and chemical properties of adamantane derivatives containing C = C double bonds are described systematically and surveyed. Dehydroadamantanes, unsaturated adamantane derivatives with an exocyclic double bond and a double bond remote from the nucleus, as well as their functional derivatives are considered. Much attention is devoted to the reactivity of unsaturated adamantane derivatives.
The bibliography includes 165 references.

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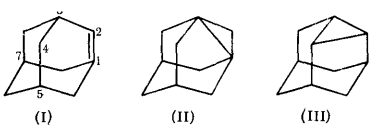
I. INTRODUCTION

The chemistry of organic polyhedranes and in the first place adamantane has developed vigorously in recent years†. Owing to their unusual properties, compounds of this class play an important role in both theoretical and experimental organic chemistry. The biological activity of organic polyhedranes has assumed considerable importance. Many medicinal drugs (rimantadine, amantidine) are at present manufactured on their basis. The high thermal stability of adamantane derivatives and their pronounced hydrophobic properties are used in the manufacture of technical products (polymeric materials, lubricating oils) with improved operational properties.

A series of reviews[1-7] and a monograph[8] have been published in recent years on the chemistry of adamantane and other polyhedranes. However, they devote little space to the chemistry of unsaturated adamantane derivatives. At the same time these compounds are of special interest primarily in view of their high reactivity; they can be used as the starting materials for the synthesis of various functional derivatives of adamantane and also as monomers. The aim of the present review is to give a systematic account and to survey the available data on the methods of synthesis and the chemical properties of adamantane derivatives containing C=C double bonds. The review includes the literature data up to 1980 inclusive and some data published in 1981–1982.

II. DEHYDROADAMANTANES

Three isomers of dehydroadamantane $C_{10}H_{14}$ are possible: 1,2-dehydroadamantane (I), 1,3-dehydroadamantane (II), and 2,4-dehydroadamantane (III):

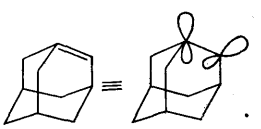


(I) (II) (III)

1,2-Dehydroadamantane belongs to the class of the so-called anti-Bredt olefins[9]. The isomers (II) and (III) can be classified as unsaturated derivatives only as a matter of convention. However, it is useful to consider them in view of the fact that, in terms of their chemical properties (primarily their high reactivity), they are extremely close to adamantane derivatives containing a multiple bond.

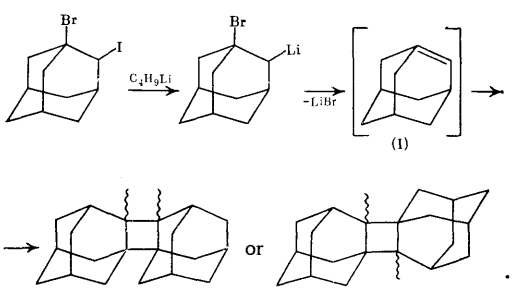
1,3-Dehydroadamantane is a strained system with two inverted carbon atoms. The 2,4-dehydroadamantane molecule is less strained and in terms of its properties is close to other alicyclic hydrocarbons containing a three-membered ring.

The possibility of the existence of 1,2-dehydroadamantane, or tricyclo[3.3.1.$1^{3,7}$]dec-1-ene, or adamantene constitutes an interesting problem in the chemistry of adamantane. Calculations have shown that adamantene is a highly strained olefin, since the overlap of the p orbitals of the C(1) and C(2) atoms, located in different planes, is difficult (a major deformation of the rigid skeleton is required). Under the usual conditions, this compound is unstable. At the same time there is much indirect evidence for its existence, 1,2-dehydroadamantane being formed as an intermediate in many reactions usually employed for the synthesis of strained olefins:



(I)

Thus bisdehalogenation of 1-bromo-2-iodoadamantane with n-butyl- or s-butyl-lithium yielded a hydrocarbon $C_{20}H_{28}$:[10]

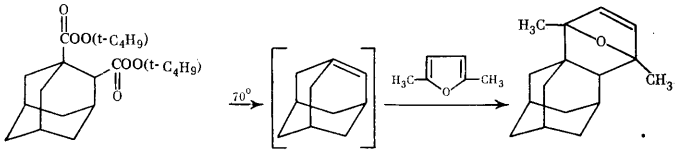


Analogous dimers have been obtained in 98% yield on treatment of 1,2-di-iodoadamantane with n-butyl-lithium in pentane at 0 °C;[11] at -80 °C in pentane in the presence of a large excess of butadiene a butadiene–adamantane adduct was isolated in addition to the dimer (85%).[12,13] When a

† During this year, 50 years have elapsed since the discovery of adamantane; it was first detected by Landa and Macháček in the petroleum of the Hodonin deposit (Czechoslovakia).

mixture of 1,2-di-iodoadamantane and lithium diphenyl phosphate is heated in tetrahydrofuran (VHF) and then oxidised with hydrogen peroxide, an adamantane dimer is also formed[14].

Adamantene is likewise produced as an intermediate in the decomposition of the di-t-butyl ester of the adamantane-1,2-dicarboxylic peracid in 2,5-dimethylfuran[15]. An adamantane–dimethylfuran adduct was then obtained by the Diels–Alder reaction:



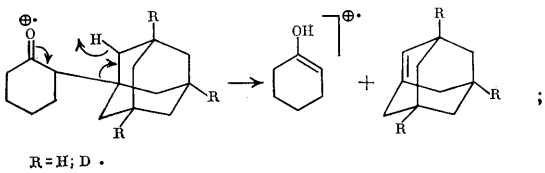
Debromination of 1,2-dibromoadamantane by treatment with $(CH_3Si)_2Hg$ in boiling benzene also leads to the formation of adamantene as an intermediate, which dimerises in the absence of acceptors and, when the reaction is carried out in the presence of 2,5-dimethylfuran, gives rise to the corresponding Diels–Alder adduct[16].

The formation of adamantene has been confirmed by spectroscopic methods. According to infrared and EPR spectroscopic data, the main product of the interaction of 1,2-dibromo- and 1,2-di-iodo-adamantane with sodium and potassium vapours stabilised in an argon matrix at 10 K is adamantene; the 1-adamantyl radical is also formed in small amounts[17]. After heating the matrix to approximately 20 °C, [2 + 2] dimers and small amounts of 1,1'-biadamantyl were detected in the reaction mixture by gas chromatography–mass spectrometry. Judging from the infrared spectroscopic data, the character of the C=C bond in adamantene is closer to that of an unstrained C=C bond than to a biradical. However, this double bond has a partial radical character, which is evident from the formation of a dimer, of which ordinary olefins are incapable[17].

The attempt to obtain adamantene by the photoelimination reaction from 1-adamantylacetone was unsuccessful[18]. At the same time the formation of adamantene from adamantyl esters (1- and 2-adamantyl phenylacetates) via the photoelimination reaction in methanol has been observed; in both cases the subsequent ionic addition of the residue of the solvent molecule to adamantene leads to the same product; 1-methoxyadamantane[19].

The formation of the adamantene ion (*m/e* 134) from 2-adamantyl trifluoroacetate has been demonstrated by the kinetic field ionisation method[20].

The ionisation of 2-(1-adamantyl)cyclohexanone on electron impact in a high vacuum (10^{-6} mmHg) leads to the formation of the 1-hydroxycyclohexenylium radical-cation and the neutral compound (I):[21]



R=H; D.

The closest cyclic homologue of adamantene is 3-homoadamantene (IV), whose strain energy is much lower in view of the greater size of the ring containing the C=C double bond (Table 1)[22]. The theoretical existence of 3-homoadamantene was predicted in a number of studies[23–25]. It was obtained in a pure form (condensed on a NaCl plate at −196 °C) by the pyrolysis of 1-adamantyldiazomethane *in vacuo* (10^{-3} mmHg, 375 °C). When compound (IV) is heated to room temperature, the 3-homoadamantene dimer is formed according to infrared spectroscopic data[26]; it has also been described in other communications[27,28]. Its pyrolysis at 500° to 520 °C leads to 3-vinylnoradamantane (V), 4-methylene-protoadamantane (VI), and 4-homoadamantane (VII):[27]

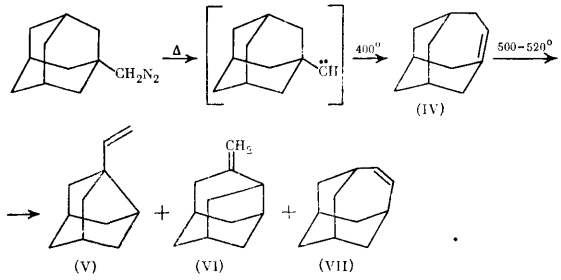


Table 1. The stability of certain olefins with a C=C bond at the base of the bridge[22].

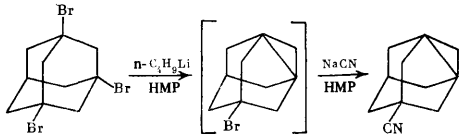
Olefin	$\Delta H°$, kcal mol^{-1}	$E°$, kcal mol^{-1}	$\Delta E°$, kcal mol^{-1}
Bicyclo[2,2,2]oct-1-ene	+42.72	50.6	40.4
Adamantene	+32.26	43.0	39.5
3-Homoadamantene	+18.92	35.3	20.2
Bicyclo[3,3,2]dec-1-ene	+6.18	25.2	4.7
Bicyclo[4,4,1]undec-1-ene	−8.95	15.7	−1.5

Note. $\Delta H°$ is the heat of formation, $E°$ the strain energy, and $\Delta E°$ the difference between the strain energies of the alkene and the corresponding alkane.

1,3- and 2,4-Dehydroadamantanes, which are entirely stable compounds, are obtained by the reactions usually employed for the synthesis of cyclopropane hydrocarbons (1,3-elimination, insertion of a carbene, etc.).

1,3-Dehydroadamantane was first synthesised by treating 1,3-dibromoadamantane with the Na–K alloy in boiling heptane; its structure was confirmed by chemical reactions involving the opening of the three-membered rings[29] A 9 : 1 mixture of 1,3-dehydroadamantane and adamantane has been obtained analogously in 77% yield from 1,3-dibromoadamantane in ether containing traces of t-butyl alcohol and (or) hexamethylphosphoramide (HMP).[30] Under these conditions, 1,3-dibromo-5,7-dimethyladamantane gives rise to a 1 : 1 mixture of 1,3-dehydro-5,7-dimethyladamantane and 1,3-dimethyladamantane in 78% yield[30].

When lithium is used, the cyclisation of 1,3-dibromoadamantane takes place in THF at room temperature. However, the presence of a catalyst, namely alkylarylchlorosilane, is required in this instance; the yield of compound (II) is 80%.[31] Treatment of 1,3,5-tribromoadamantane with n-butyl-lithium at −35 °C in ether containing HMP (in proportions of 25 : 1) leads to 5-bromo-1,3-dehydroadamantane, which is converted into the stable 5-cyano-1,3-dehydroadamantane following the addition of NaCN:[32]



The formation of compound (II) is also observed in the polarographic reduction of 1,3-dibromoadamantane[33].

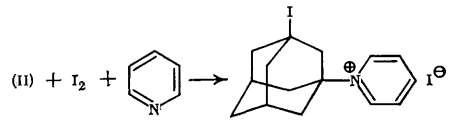
Like other alicyclic hydrocarbons containing a strained three-membered ring, 1,3-dehydroadamantane and its derivatives are very reactive. The C(1)–C(3) bond in compound (II) is greatly weakened; its length is 1.64 Å while the lengths of other C–C bonds in adamantane are 1.53 Å [Majerski et al.[5] (p.37)]. Because of this, the reactions of 1,3-dehydroadamantane proceed selectively with the opening of the three-membered ring and the formation of 1-mono- or 1,3-di-substituted derivatives of adamantane; the fragmentation of the adamantane ring also takes place sometimes.

The oxidation of compound (II) with air at 20 °C in heptane leads to a peroxide, which decomposes explosively at 160 °C.[29] In air and in solution in pentane at room temperature, compound (II) is converted into a mixture of copolymers with oxygen, whose main component is the explosive polyperoxyadamantane $(OC_{10}H_{14}O)_n$.[29,30]

On heating (130–160 °C) in a sealed tube, compound (II) is converted into a white polymer (1,3-polyadamantane) having the composition $(C_{10}H_{14})_n$, which is insoluble in organic solvents and is stable in an atmosphere of nitrogen at 400 °C. An analogous polydimethyladamantane is formed from 1,3-dehydro-5,7-dimethyladamantane at 90–145 °C. In the absence of oxygen, compound (II) is thermally stable, its half-life at 195 °C in solution in n-octane amounting to approximately 4 h.[29,30]

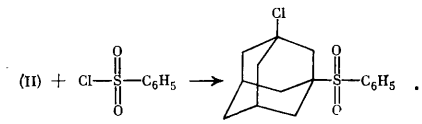
Catalytic hydrogenation of compound (II) leads to adamantane in 82% yield and the interaction of compound (II) with bromine or iodine gives rise to 1,3-dibromo- and 1,3-di-iodo-adamantane respectively[29].

Treatment of compound (II) with iodine in the presence of pyridine produces *N*-(3-iodo-1-adamantyl)pyridinium iodide[34]:

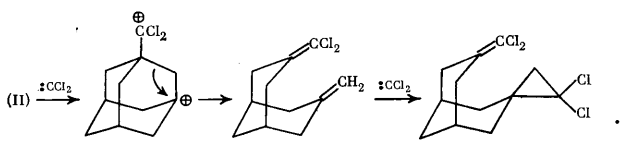


This reaction is one of the first examples of coupled intermolecular halogenoamination.

1,3-Dehydroadamantane combines with benzenesulphonyl halides even in the absence of a catalyst[35]:

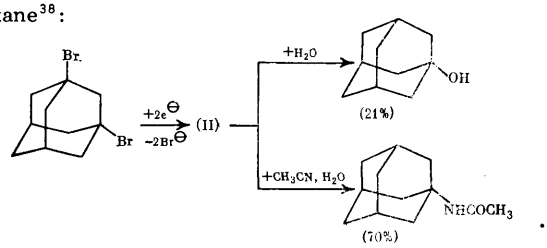


Under the conditions of the catalytic generation of dichlorocarbene, 1,3-dehydroadamantane combines with two equivalents of the carbene to form 7-dichloromethylenebicyclo[3.3.1]nonane-3-spiro-1-(2',2'-dichloro)cyclopropane[36]:



The reaction of compound (II) with aryliodosocarboxylates having the general formula $ArI(OCOR)_2$, where R = alkyl or aryl, has been investigated[37]. The main products of this reaction in inert solvents at room temperature are iodobenzene and 1,3-diacyloxyadamantenes.

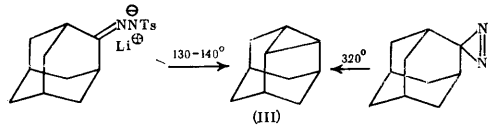
1,3-Dehydroadamantane is formed in the electrochemical reduction of 1,3-dibromoadamantane in acetonitrile at a mercury electrode. It reacts with acetonitrile and the water contained in it to form 1-adamantanol and 1-acetamidoadamantane[38]:



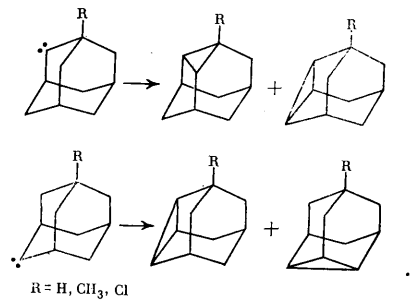
The addition of acetic acid to compound (II) leads to 1-adamantyl acetate[39].

The reaction of compound (II) with maleic anhydride, acrylonitrile, and dimethyl acetylenedicarboxylate results in the formation of oligomeric products[40]. The reactions are carried out at room temperature and in the absence of polymerisation initiators; the homopolymerisation of each monomer takes place under more severe conditions.

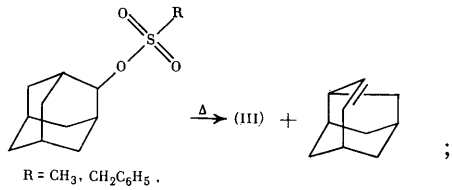
2,4-Dehydroadamantane or tetracyclo[4.3.1.$0^{2,4}$.$0^{3,8}$]decane is an extremely stable compound (m.p. 202.5–203.5 °C). In a pure form, compound (III) has been obtained by the pyrolysis of the dry lithium salt of 2-adamantanone *p*-tosylhydrazone at 130–140 °C (yield 65%)[41] and adamantane-2-spiro-3'-diazirine at 320 °C (yield 96%):[42]



Derivatives of 2,4-dehydroadamantane containing bridgehead substituents have been obtained recently by the hydrolysis of the corresponding alkali metal salts of tosylhydrazones#. It was established that the proportions of the products of the intramolecular insertion of the intermediate carbenes in the C–H bond depend on the substituent and its position relative to the carbene centre:



The pyrolysis of adamantane-2-sulphonate at 520 °C leads to compound (III) and protoadamantene (in 57 and 38% yields respectively):[43]



S.Hiršl-Starčevič and Z.Majerski, J.Org.Chem., 1982, **47**, 2520.

Irradiation of solutions of 2-iodo- and 2-bromo-adamantanes with ultraviolet light leads to a mixture of adamantane, compound (III), protoadamantene and respectively (depending on the solvent employed) 2-ethoxy- or 2-methoxy-adamantane[44]. The last two compounds are obtained as a result of the nucleophilic attack by solvent molecules on the intermediate 2-adamantyl cation; the deprotonation of the cation leads to a mixture of compound (III) and protoadamantene:

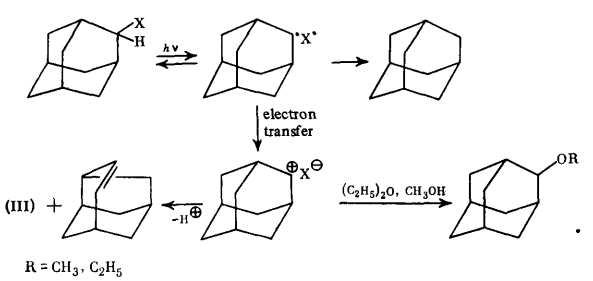
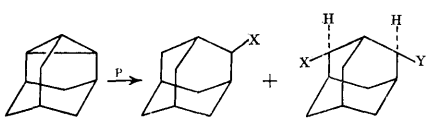


Table 2. 2-Substituted adamantanes formed on interaction of 2,4-dihydroadamantane with electrophiles[45].

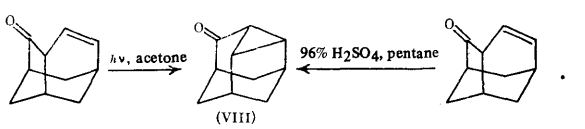
Reagents P	Substituent X	Yield, %
HI	I	24
CH_3COOH, H_2SO_4	$OCOCH_3$	94
CH_3OH, BF_3	OCH_3	80
C_6H_6, $AlCl_3$, BF_3	C_6H_5	70
$C_6H_5CH_3$, $AlCl_3$, BF_3	$C_6H_4CH_3$	50
$C_6H_5OCH_3$, $AlCl_3$, BF_3	$C_6H_4OCH_3$	86

The availability of 2,4-dehydroadamantane provides a unique possibility for the synthesis from it of 2-mono- and 2,4-di-substituted adamantane derivatives, which are otherwise difficult to obtain, as a result of the opening of the three-membered ring by electrophiles (Tables 2 and 3).[45,46] The reactions of compound (III) with such reagents (P) proceed in accordance with the following general mechanism:



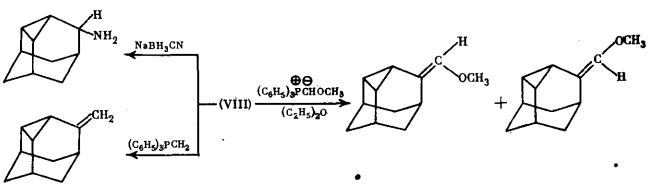
The oligomerisation of compound (III) under the influence of $AlCl_3$ leads to a dimer and a trimer; higher oligomers have not been detected in the reaction products[47]. It has been suggested that the oligomerisation proceeds via an ionic chain mechanism with the intermediate formation of the 1-adamantyl cation.

The 2,4-dehydroadamantane derivative (VIII) has been obtained by the photoisomerisation[48,49] of 2-protoadamantenone or its isomerisation in the presence of an acid catalyst[50]:



Compound (VIII) has been synthesised in several stages from norbornadiene with an overall yield of 2%.[51] It is readily converted into compound (III) by the Wolff–Kishner reaction in 75% yield[52].

The presence of the active carbonyl group permits the synthesis of other 2-substituted 8,9-dehydroadamantanes from compound (VIII):[48]



2,4-Methano-2,4-dehydroadamantane, which is the closest cyclic homologue of 2,4-dehydroadamantane, has been obtained by the pyrolysis of the dry sodium salt of 4-methylene-2-adamantanone tosylhydrazone[53], is relatively stable at room temperature, and reacts rapidly with oxygen, methanol, and bromine to form a complex mixture of products. The structure of this propellane has been demonstrated by ^{13}C NMR.[54]

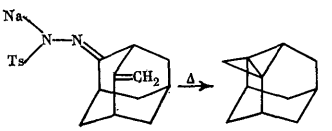
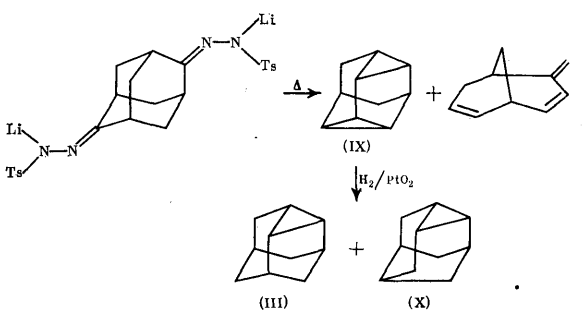


Table 3. 2,4-Disubstituted adamantanes formed on interaction of 2,4-dehydroadamantane with electrophiles[45].

Reagents P	Substituents		Yield, %
	X	Y	
Cl_2, CCl_4	Cl	Cl	77
Br_2, CCl_4	Br	Br	86
I_2, CCl_4	I	I	100
Cl_2, CH_3CN, H_2O	Cl	$HNCOCH_3$	76
Br_2, CH_3CN H_2O, $AgClO_4$	Br	$HNCOCH_3$	78
I_2, CH_3CN, H_2O, $AgClO_4$	I	$HNCOCH_3$	81
Cl_2, H_2O, $(C_2H_4O)_2$	Cl	OH	71
N-Bromosuccinimide, H_2O	Br	OH	83
C_3H_5OH, H_2O, $AgNO_3$	OH	OH	50
CH_3OH, *N*-bromosuccinimide	Br	OCH_3	23
$Hg(CH_3COO)_2$, H_2O	OH	$HgOCOCH_3$	95
NOCl, $CHCl_3$	Cl	NOH	38

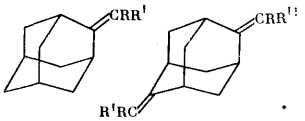
2,4,6,9-Tetradehydroadamantane (IX) or pentacyclo-[4.4.0.$0^{2,10}$.$0^{3,5}$.$0^{4,8}$]decane is of considerable interest. It is a stable compound, melting at 152–154 °C and capable of withstanding heating to 250 °C for 10 min without change of structure. It has been obtained by the thermolysis of the dilithium salt of 2,6-adamantanedione bistosylhydrazone[55,56]:



Catalytic hydrogenation of compound (IX) over a platinum catalyst at room temperature and atmospheric pressure in the presence of THF and acetic acid results in the cleavage of only one cyclopropane ring with formation of a mixture of two $C_{10}H_{14}$ hydrocarbons: 2,4-dehydroadamantane and, mainly, dehydroprotoadamantane (X) or tetracyclo[4.4.0. .$0^{2,10}$.$0^{4,8}$]decane. Compound (IX) does not isomerise under the influence of temperature and a catalyst (80 °C, $AgBF_4$).[56]

III. ADAMANTANE DERIVATIVES CONTAINING AN EXOCYCLIC C=C DOUBLE BOND

By virtue of the characteristic features of the adamantane structure, an exocyclic π-bond is possible only in a bridging position in the nucleus:

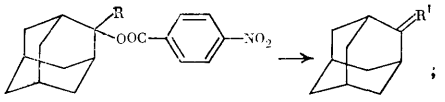


(XI) (XII)

Compounds of type (XI) are as a rule obtained by the traditional method—the dehydration of the corresponding tertiary alcohols produced by the condensation of adamantanone and lithium alkyls or Grignard reagents. In particular, 2-methyleneadamantane[57,58], 2-ethylideneadamantane[60,61], 2-propylideneadamantane[60], 2-isobutylideneadamantane[60], and 2-butylideneadamantane[60,62] have been obtained in this way.

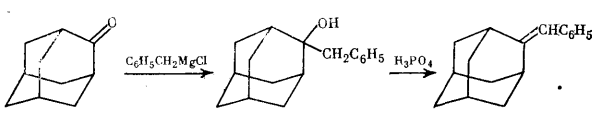
Certain derivatives of unsaturated compounds of type (XI) such as 2-hydroxy-6-methyleneadamantane[65], 6-ethylidene-2-methyladamantane or 6-propylideneadamantane[68], and 8-methylene- and 8-isopropylidene-2,6-dioxa-adamantanes[69] are also obtained by the dehydration of the corresponding alcohols. Iodine is the best dehydrating agent[63], since acid catalysts can lead to the formation of side products, as happens, in particular, on heating 2-methyl-2-adamantanol with phosphoric acid[58,64]. When 2-methyl- and 2-isopropyl-2-adamantanols are treated with acetic anhydride, methyleneadamantane and a mixture of isopropylideneadamantane with isopropenyladamantane are obtained respectively[65]. Refluxing of 2-isopropyl-2-adamantanol and 2-isopentyl-2-adamantanol in xylene in the presence of I_2 resulted in the formation of isopropylideneadamantane and isopentylideneadamantane respectively[63].

Another way of obtaining these olefins involves the solvolysis of 2-alkyl-2-adamantyl *p*-nitrobenzoates[59]:

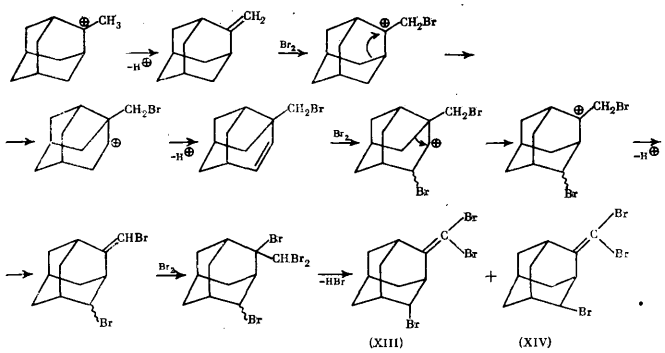


R = CH_3, C_2H_5, $CH_2C(CH_3)_3$, iso-C_3H_7;
R' = CH_2, $CHCH_3$, $CHC(CH_3)_3C(CH_3)_2$.

There are data concerning the synthesis of di-t-butylmethyleneadamantane by the thermolysis of the corresponding adamantane-2-spiro-thiadiazoline[66]. Benzylideneadamantane has been obtained in 90% yield by the dehydration of 2-benzyl-2-adamantanol in the presence of a tenfold excess of 85% orthophosphoric acid at 120 °C:[67]



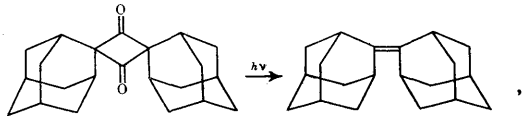
Bromo-derivatives of 2-methyleneadamantane (XIII) and (XIV) have been obtained as a result of the unusual course of the bromination of 2-methyladamantane[70]:



(XIII) (XIV)

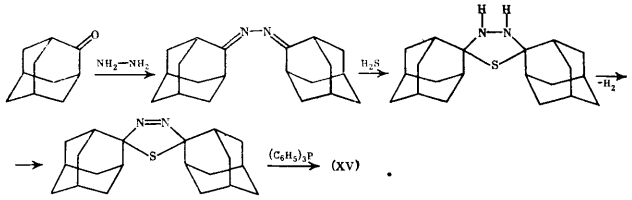
ω-Bromomethyleneadamantane has been synthesised by brominating methyleneadamantane with *N*-bromosuccinimide in the presence of Br_2O_2 or by the Wittig reaction from 2-adamantanone and $(C_6H_5)_3P{=}CHBr$.[71]

Adamantylideneadamantane (XV) is of significant interest; it is formed by the photochemical decarbonylation of the 2-adamantylketen dimer[72],

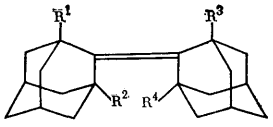


(XV)

and the debromination of *gem*-2-dibromoadamantane with the aid of the zinc–copper couple[73]. Compound (XV) has also been synthesised in accordance with the following scheme[74]:



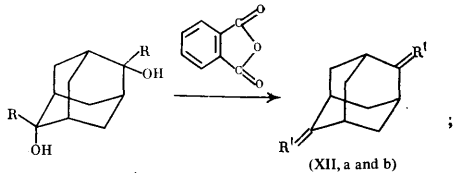
Many methyl derivatives of adamantylideneadamantane (XV, a–e) have been synthesised too[75,76]:



(XVa-e)

(a) R^1, R^2, R^3, R^4 = H;
(b) R^1, R^4 = H, R^2, R^3 = CH_3;
(c) R^1, R^3 = H, R^2, R^4 = CH_3;
(d) R^1, R^2 = H, R^3, R^4 = CH_3;
(e) R^1, R^2, R^3, R^4 = CH_3.

The bisunsaturated derivatives of adamantane of type (XII) have been obtained by the dehydration of the corresponding diols[77]:

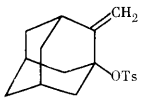


(XII, a and b)

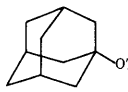
(a) R = CH_3, R' = CH_2 (45%);
(b) R = C_2H_5, R' = C_2H_4 (90%).

In terms of their chemical properties, unsaturated derivatives of adamantane of types (XI) and (XII) are close to other alicyclic hydrocarbons containing an isolated exocyclic C=C double bond. The catalytic hydrogenation of hydrocarbons of types (XI) and (XII) leads to 2-alkyl- and 2,6-dialkyl-adamantanes[77]: on reaction with methylene iodide in the presence of the zinc-copper couple or with diazomethane in the presence of copper bromide, methylene- and ethylidene-adamantanes give rise to the corresponding cyclopropane derivatives[78]: methyleneadamantane combines with dichloro- and dibromo-carbenes to form 2,2-dichloro- and 2,2-dibromo-(2-adamantyl)spiro-1'-cyclopropanes[79].

At the same time the presence of the bulky adamantyl group gives rise to major steric hindrance, which reduces the reactivity of the C=C bond and the rigidity of the structure prevents the appearance of the possible conjugation effects. Thus, as a consequence of the hindrance to the conjugation between the cationic centre and the adjoining double bond in 2-methylene-1-adamantanyl tosylate, the rate of solvolysis of the tosylate (XVI) is lower than that of the unsubstituted tosylate (XVII) by a factor of 10^4, although the opposite relation might have been expected[80]:

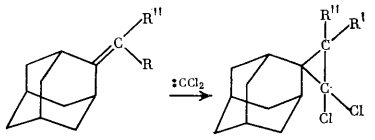


(XVI)



(XVII)

The reactivity of the double bonds of the olefins (XI) in the reactions with dichlorocarbene depends significantly on the size and character of the substituent[81]:

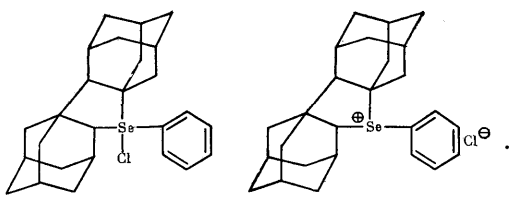


(XI)

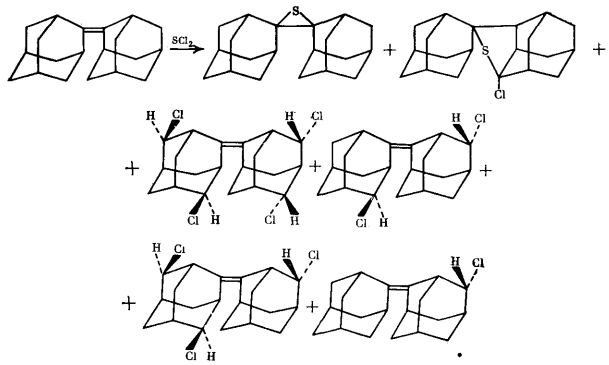
R' = R'' = H; R' = CH_3, R'' = H; R' = C_2H_5, R'' = H; R' = $(CH_3)_2CH$, R'' = H; R' = $(CH_3)_2CHCH_2$, R'' = H; R' = C_6H_5, R'' = H; R' = R'' = CH_3; R' = R'' = C_6H_5. The groups R' and R'' increase (primary alkyl groups) or decrease (isopropyl and phenyl groups) the reactivity of the double bond in conformity with the manifestation of the inductive and steric effects by the latter. The hydrocarbon (XI, R' = R'' = C_6H_5) does not react with dichlorocarbene.

Steric effects are shown particularly strikingly for adamantylideneadamantane. When compound (XV) was halogenated, its stable complexes with chlorine and bromine were isolated[82,83]. On the basis of ^{13}C NMR investigations, the structure of two-electron three-centre π-complexes was attributed to them[84].

The unique behaviour of the double bond of compound (XV) permits the synthesis of thermally stable complexes[85]:



The reaction of SCl_2 with the highly hindered double bond in compound (XV) proceeds in an unusual manner and, depending on the reaction conditions, results in the formation of compounds containing S-heterocycles and also chloro-substituted adamantylideneadamantanes[86,87]:



The reaction of compound (XV) with $MoOCl_4$ or $SbCl_5$ in the presence of Lewis acids leads respectively to adamantylideneadamantanechloronium heptachlorodioxodimolybdate and hexachloroantimonate[88]:

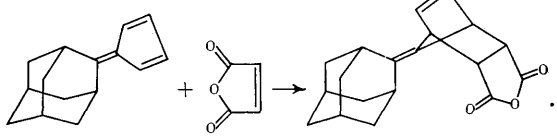
$$2MoOCl_4 + A{=}A \rightarrow [A(Cl)A]^{\oplus}\,[Mo_2O_2Cl_7]^{\ominus},$$

$$2\,SbCl_5 + A{=}A \rightarrow [A(Cl)A]^{\oplus}\,[SbCl_6]^{\ominus} + SbCl_3,$$

where A = 2-adamantylidene.

As a result of the considerable hindrance of the double bond, the addition of dichlorocarbene to compound (XV) takes place twenty times more slowly than to the hydrocarbon (XI, R' = R'' = H).

2-Cyclopentadienylideneadamantane (XVIII), which can be readily obtained from 2-adamantanone and cyclopentadiene, has interesting synthetic possibilities[89]. Its hydrogenation leads to 2-cyclopentenyl- and 2-cyclopentyl-adamantanes[89,90]. The hydrocarbon (XVIII) enters actively into condensation reactions with dienophiles, for example[91]:



(XVIII)

IV. ADAMANTANE DERIVATIVES WITH A C=C DOUBLE BOND IN A SIDE CHAIN

The adamantane derivatives belonging to this group include compounds containing an unsaturated substituent at both bridgehead and bridging positions, as well as compounds having two (identical or different) substituents in the 1- and 3-positions. Traditional methods are usually employed successfully for their synthesis, although some exceptions are known. Thus, despite the wide-scale variation of the reaction conditions in the dehydration of 1-(1-hydroxyethyl)-adamantane, 1-vinyladamantane (XIX) could not be obtained[92]. The attempt to synthesise compound (XIX) by the pyrolysis of a quaternary ammonium base, namely 2-(1-adamantyl)-ethyltrimethylammonium hydroxide, was also unsuccessful[93].

1-Vinyladamantane was first synthesised by the dehydration of 1-ethyladamantane in the presence of a catalyst containing aluminium and chromium, molybdenum, and tungsten hydroxides[94]. A patent was later published[95] in which several methods for the dehydration of 1-(1-hydroxyethyl)-adamantane are described. Compound (XIX) has been obtained in the highest yields (85–95%) by the pyrolysis of the borate and acetate derived from the initial alcohol. The yield of compound (XIX) in the dehydration of the unsubstituted alcohol over alumina at 350–400 °C did not exceed 30%.

The thermal cleavage of 2-(1-adamantyl)ethyl *S*-methyl xanthate leads to compound (XIX) in 77% yield[93] §:

$$AdCH_2CH_2OC(=S)SCH_3 \xrightarrow{270^\circ} AdCH{=}CH_2 + S{=}C(OH)SCH_3$$
(XIX)

Compound (XIX) has been synthesised in 80% yield by the dehydration of the borate of 1-(2-hydroxyethyl)adamantane at 300 °C.[96] 1-(Vinyl)adamantane is the product of the debromination (with Zn in dimethylformamide) of 1-adamantyl-1,2-dibromoethane[97,98].

The interaction of adamantane with acetylene under the influence of ^{60}Co γ-radiation also leads to compound (XIX) in 8% yield[99]. This method cannot evidently have any preparative value, although it is of interest as the first example of the formation of 1-vinyladamantane via a radical chain mechanism.

A procedure has been proposed recently for the synthesis of 1-vinyladamantane homologues by the reaction of 1-propenyladamantanes with ethylene in the presence of an alumina–rhenium heptoxide catalyst (10–20% Re_2O_7 and 80 to 90% Al_2O_3) at 20 °C and atmospheric pressure[100].

Propenyladamantanes are formed when adamantane and its homologues react with propene over industrial alumina and zeolite-containing catalysts[101]. If the starting material is 1-adamantanol, trifluoroacetic acid can also be used as the catalyst[102,103].

Regardless of the method of preparation of 1-propenyladamantane (XX), its formation is accompanied by that of its isomer—1-allyladamantane (XXI). In the dehydrohalogenation of 1-(2-bromopropyl)adamantane, the contents of compounds (XX) and (XXI) in the reaction mixture are 80 and 7.4 respectively[104]:

$$AdCH_2CHBrCH_3 \rightarrow \underset{(XX)}{AdCH{=}CHCH_3} + \underset{(XXI)}{AdCH_2CH{=}CH_2}$$

The products of the pyrolysis of 1-(1-adamantyl)-2-propyl acetate contain 70% of compound (XX) and 30% of compound (XXI).[105] Compound (XX) is probably thermodynamically more stable.

1-Allyladamantane has been synthesised by the debromination of 3-(1-adamantyl)-1,2-dibromopropane with zinc in boiling ethanol in 89% yield[104], and also by the reaction of 1-chloroadamantane with $CH_2{=}CHCH_2SI(CH_3)_3$ with participation of Lewis acids ($TiCl_4$).[106,107]

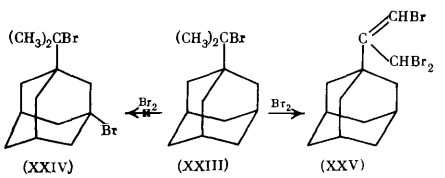
1-Isopropenyladamantane (XXII) has been synthesised by the dehydration of a tertiary alcohol—2-(1-adamantyl-2-propanol—by acetic anhydride[108] or iodine[109]:

$$AdC(CH_3)_2OH \rightarrow \underset{(XXII)}{AdC(CH_3){=}CH_2}$$

When an attempt was made to synthesise t-butyladamantane from 2-(1-adamantyl)-2-propanol, the main product was also compound (XXII):[110]

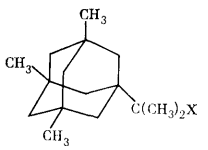
$$AdC(CH_3)_2OH \xrightarrow{SOBr_2} AdC(CH_3)_2Br \xrightarrow{CH_3MgI} AdC(CH_3)_3$$
$$\rightarrow \underset{(XXII)}{AdC(CH_3){=}CH_2} \leftarrow$$

Unsaturated derivatives of the type considered are likewise formed in halogenation reactions. Thus, instead of the expected bromo-derivative (XXIV), the unsaturated tribromo-derivative (XXV) is obtained on bromination of 2-(1-adamantyl)-2-bromopropane (XXIII):[111]



(XXIV) (XXIII) (XXV)

Bromination of compounds (XXVI) and (XXVII) proceeds analogously, i.e. with formation of unsaturated products[111]:



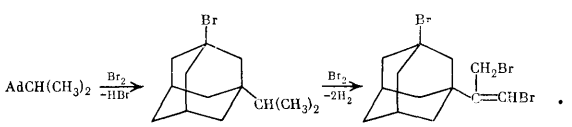
(a) X = Br (XXVI)
(b) X = H (XXVII)

In conformity with the proposed reaction mechanism, the C=C bond is formed on deprotonation of the intermediate carbonium ions[111], as in the bromination of 2-methyladamantane considered above[70]:

$$AdC(CH_3)_2Br \xrightarrow[-Br_3^\ominus]{+Br_2} AdC^\oplus(CH_3)_2 \xrightarrow{-H^\oplus} AdC(CH_3){=}CH_2 \xrightarrow{+Br_2}$$
$$\rightarrow AdC(CH_3)BrCH_2Br \xrightarrow[-2H^\oplus,\,-Br_3^\ominus]{+Br_2} \underset{CHBr_2}{AdC^\oplus CH_2Br} \xrightarrow{-H^\oplus} \underset{CHBr_2}{AdC{=}CHBr}$$

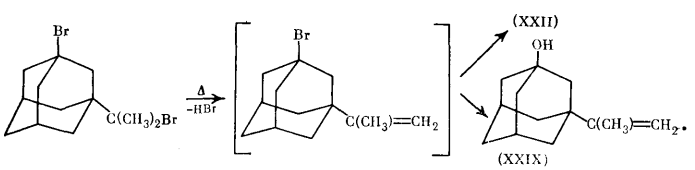
An analogous mechanism operates in all probability in the alkenylation of adamantane by propene[101].

1-Isopropyladamantane is usually brominated exclusively in the nucleus, forming 1-bromo-3-isopropyladamantane. However, on increasing the reaction time under the conditions adopted [95–100 °C, $AdCH(CH_3)_2 : Br_2 = 1 : 22$], further bromination takes place with formation of compound (XXVIII):[112]



(XXVIII)

Thermal dehydrobromination of 2-bromo-2-(3-bromo-1-adamantyl)propane results in the formation of a monobromide, which is converted into the olefin (XXII) and the unsaturated alcohol (XXIX)[113] (p.75):



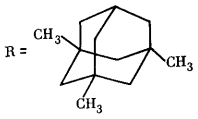
(XXIX)

Fluoro-substituted alkenyladamantanes, which are of great practical interest, are obtained by the dehydrofluorination reaction. Thus dehydrofluorination of 1-hexafluoropropyladamantane in the presence of $C_2H_5OH/NaOH$ leads to 1-pentafluoropropenyladamantane in 75% yield[114]. Spectroscopic data demonstrate the presence of a double bond in the vinyl position.

§ Here and henceforth Ad = 1-adamantyl.

1-Isopropenyl-3,5,7-trimethyladamantane (XXX) has been synthesised[113] by the dehydration of the corresponding alcohol, which was obtained from methyl 3,5,7-trimethyladamantane-1-carboxylate (XXXI):

$$\underset{\text{(XXXI)}}{RC(O)OCH_3} \xrightarrow{CH_3MgI} RC(CH_3)_2OH \xrightarrow{-H_2O} \underset{\text{(XXX)}}{RC(CH_3)=CH_2};$$



1-Isopropenyl-2-methyladamantane is a product of the dehydration of 2-(2-methyl-1-adamantyl)-2-propanol by acetic anhydride[115].

1-(1-Adamantyl)-2-methyl-2-propanol has been used to synthesise the butenyladamantanes (XXXIII) and (XXXIV).[116] The dehydration takes place both on heating the alcohol with acetic anhydride[115] or anhydrous oxalic acid[105] and on treatment of the alcohol with hydrogen bromide in glacial acetic acid[105,116]. Evidently, the conversion of the alcohol takes place in two stages—via the intermediate formation of the tertiary carbonium ion (XXXII), which is stabilised as a result of the electron-donating effect of the adamantane nucleus:

$$AdCH_2C(CH_3)_2OH \xrightarrow{HBr,CH_3COOH} \underset{\text{(XXXII)}}{AdCH_2\overset{\oplus}{C}(CH_3)_2} \begin{cases} \xrightarrow{-H^{\oplus}} \underset{\text{(XXXIII)}}{AdCH_2C(CH_3)=CH_2} + \underset{\text{(XXXIV)}}{AdCH=C(CH_3)_2} \\ \longrightarrow \overset{\oplus}{Ad} + CH_2=C(CH_3)_2 \end{cases}.$$

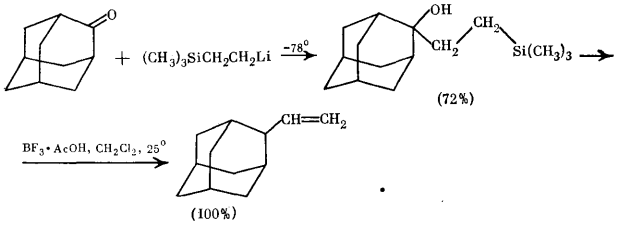
Further reactions of the ion (XXXII) take place with formation of the more stable 1-adamantyl cation as an electrophilic fragment or with elimination of the proton and the formation of unsaturated compounds.

1-(1-Adamantyl)-2-chloro-2-phenylethylene (XXXV) has been synthesised from 1-chloroadamantane[106,107]:

$$AdCl + C_6H_5C{\equiv}CSi(CH_3)_3 \xrightarrow{TiCl_4} \underset{\text{(XXXV)}}{AdCH=CClC_6H_5}.$$

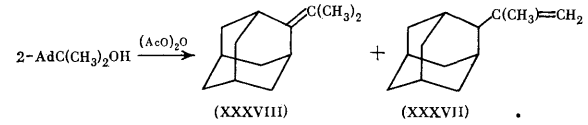
To confirm the structure of compound (XXXV), $C_6H_5CH=$CHAd (XXXVI) was synthesised by the Wittig reaction from adamantane-1-carboxyaldehyde and $C_6H_5CH=P(C_6H_5)_3$. The reduction of compound (XXXV) by zinc in boiling alcohol leads to *cis*-(XXXVI).

Adamantanes with an unsaturated side chain in the 2-position have been hardly investigated. 2-Vinyladamantane can be obtained in a high yield by the direct conversion of adamantanone under the influence of β-[(trimethylsilyl)ethyl]-lithium¶:

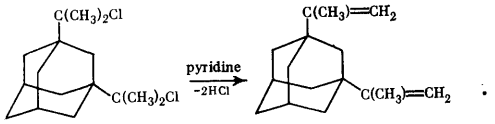


¶ S.R.Wilson and A.Shedrinsky, J.Org.Chem., 1982, **47**, 1983.

The formation of 2-isopropenyladamantane (XXXVII) in a 1 : 4 mixture with 2-isopropylideneadamantane (XXXVIII) on dehydration of 2-(2-adamantyl)-2-propanol has been noted[65]:



Adamantanes containing two unsaturated substituents in the molecule have been obtained by analogous methods. Thus 1,3-di-isopropenyladamantane has been synthesised by the dehydrochlorination of a dichloro-derivative[117]:



1-Allyl-3-vinyladamantane and 1,3-diallyladamantane have been obtained by the dehydrobromination of the corresponding bromo-derivatives[104].

Unsaturated hydrocarbons of the adamantane series, containing the double bond in the α-position in the side chain, are as a rule liquids with boiling points above 200 °C, which are fairly stable on heating. A study of the mass spectra of these compounds has shown that their molecular ions (M^+) are much more stable than the M^+ derived from the corresponding alkyladamantanes (the M^+ intensities for 1-ethyl- and 1-vinyl-adamantanes are 4 and 92% respectively)[118,119]. The intensity of the ions with *m/e* 135 (or their homologues), corresponding to the elimination of alkenyl groups, is low. These data indicate the greater stability of the C_{ad}–C_{alk} bond in alkenyl adamantanes than in alkyladamantanes. This may be the result of the interaction of the C=C bond with the excess electron density within the adamantane nucleus (1,3-conjugation); such conjugation can arise as a result of the overlap within the skeleton of the rear portions of the orbitals of the four bridgehead carbon atoms (a cage effect is postulated—see, for example, Fort[8] (p.161). However, such interaction, if it does in fact occur, is energetically insignificant, since its appreciable influence on the chemical properties of the compounds has not been observed. Thus 1-vinyladamantane and 1-allyladamantane have the same reactivities in relation to iodine[120]. The hydrogenation of these olefins gave high yields (80–95%) of the corresponding alkyladamantanes[93,105,116]. 1-Vinyladamantane usually combines with HBr according to the Markovnikov rule[93]. However, under certain conditions the main product of the addition of HBr to 1-vinyladamantane is 1-(1-adamantyl)-2-bromoethane and not 1-(1-adamantyl)-1-bromoethane (XXXIX):[121]

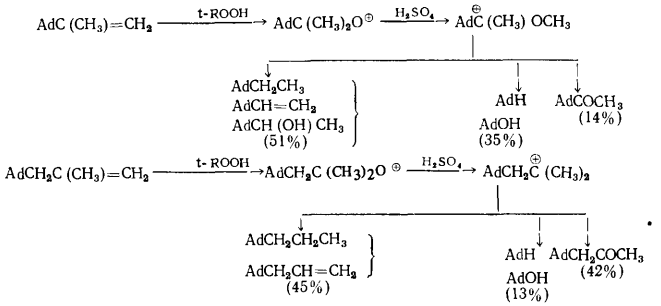
$$\underset{\delta^{\ominus}}{AdCH}=\underset{\delta^{\oplus}}{CH_2} \xrightarrow{H^{\oplus}(HBr)} AdCH_2\overset{\oplus}{C}H_2 \rightarrow AdCH(\overset{\oplus}{C})CH_3 \xrightarrow{Br^{\ominus}} \underset{\text{(XXXIX) (27\%)}}{AdCHBrCH_3}$$
$$\xrightarrow{Br^{\ominus}} \underset{\text{(73\%)}}{AdCH_2CH_2Br}.$$

The addition of bromine to 1-vinyladamantane yields 1-(1-adamantyl)-1,2-dibromoethane, the dehydrobromination of which leads to a mixture of unsaturated compounds[121]:

$$AdCH=CH_2 + Br_2 \rightarrow AdCHBrCH_2Br \xrightarrow[5h,\ reflux]{C_2H_5OH+KOH}$$
$$\rightarrow \underset{(59\%)}{AdCBr=CH_2} + \underset{(34\%)}{\textit{trans}\text{-}AdCH=CHBr} + \underset{(7\%)}{AdC{\equiv}CH}.$$

The epoxidation of 1-vinyladamantane has been achieved with the aid of t-butyl hydroperoxide in the presence of $Mo(CO)_6$; 1-epoxyadamantane has been polymerised with the opening of the epoxide ring[122].

The introduction of the adamantane nucleus into tertiary hydroperoxides should influence significantly their rearrangement in an acid medium, because a high tendency towards the formation of a cation is a distinctive feature of adamantane derivatives. Thus the hydroperoxides obtained from 1-isopropenyl- and 1-isobutenyl-adamantanes in 70% H_2SO_4 in the presence of cyclohexane give rise to a complex mixture of products[123]:



The interaction of 1-isopropenyl- and 2-isopropenyl-adamantanes[124] or 3-bromo-1-isopropenyladamantane[125] with methylene iodide in the presence of the zinc–copper couple or with diazomethane in the presence of copper bromide results in the formation of the corresponding cyclopropane derivatives, whose hydrogenolysis leads to alkyladamantanes.

Unsaturated adamantane derivatives are active in the 1,3-dipolar cycloaddition of nitrile *N*-oxides[120]. The reactivities of the unsaturated compounds investigated vary in the sequence

$$AdCH{=}CH_2 \cong AdCH_2CH{=}CH_2 > AdC(CH_3){=}CH_2 > AdC{\equiv}CH\ .$$

The decrease of reactivity in this sequence can be accounted for partly by the influence of steric factors.

Unsaturated hydrocarbons of the adamantane series can be polymerised. Thus the polymer of 1-allyladamantane has been obtained in 12.5% yield in the presence of a Ziegler–Natta catalyst. The copolymerisation of 1-allyladamantane with vinylcyclohexane led to a copolymer in 10% yield[104]. The kinetics of the copolymerisation of 3,5-dimethyl-1-vinyladamantane with vinyl acetate have been investigated[126].

The cationic polymerisation of 1-vinyladamantane takes place in anhydrous solvents under the influence of AlX_3 (X = Cl or Br);[127,128] the temperature of the onset of the decomposition of poly-1-vinyladamantane is 300 °C.[96] The use of other catalysts of the type of Lewis acids (boron trifluoride etherate, triethyloxonium fluoroborate) does not lead to the formation of a polymer.

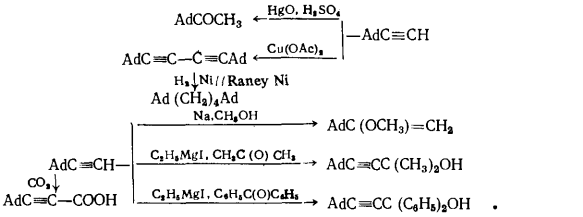
$$AdCH{=}CH_2 \xrightarrow{AlCl_3} AdCH_2CH_2{-}[{-}CH(Ad)CH_2{-}]_n{-}CH(Ad)CH_2Cl\ .$$

It has been established for the unsaturated adamantane derivatives

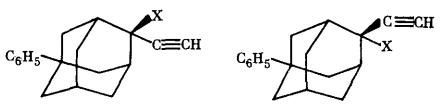
$$CH_2{=}C(CH_3)C(O)O(R)AdX;\quad CH_2{=}CH{-}O(O)C(R)AdX;$$
$$X{=}H,\ Br,\ C(O)OCH_3;\qquad R{=}(CH_2)_n,\ n = 0-2\ ,$$

that the introduction of the adamantyl group into monomers not only does not inhibit their polymerisation but in some cases leads to an increase of their capacity for polymerisation. In the series of methacrylic derivatives of adamantanes and the vinyl esters of adamantanecarboxylic acid, the type of variation of the polymerisation constants shows that, with increase of the distance between the adamantane nucleus and the double bond, the capacity of the monomers for polymerisation diminishes[129–131]. Thermal stability, resistance to hydrolysis, and enhanced surface hardness are distinctive properties of the polymers based on these adamantane derivatives.

1-Ethynyladamantane has been synthesised by the reaction of AdBr with vinyl bromide in the presence of $AlBr_3$ and subsequent dehydrohalogenation of the 1-(1-adamantyl)-1,2-dibromoethane formed by KOH in diethylene glycol[132]. 1-Ethynyladamantane undergoes many reactions characteristic of acetylenic hydrocarbons[132]:

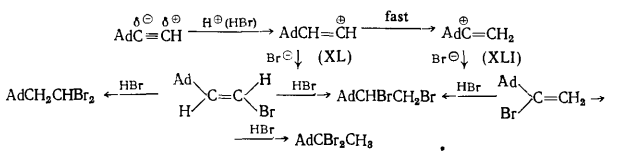


Derivatives of 2-ethynyladamantane have also been synthesised[133]:



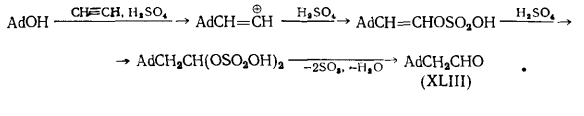
X = Cl; X = OH.

It has been suggested that the reactions of AdBr and AdOH with acetylene in concentrated sulphuric acid[135–138] and of 1-ethynyladamantane with 90% sulphuric acid[139] and with HBr in glacial acetic acid[134] proceed via the intermediate formation of adamantylvinyl cations (XL), which readily isomerise to the more stable cations (XLI). The reaction pathways of the cations (XL) and (XLI), which depends on the source from which (XL) is obtained (AdX + HC≡CH or AdC≡CH), the nature of the leaving group X (Br or OH) in AdX, and the degree of substitution in the adamantane nucleus, determine the composition of the reaction products. Thus 1-ethynyladamantane combines with HBr in glacial acetic acid to form a mixture of all the possible products[134]:



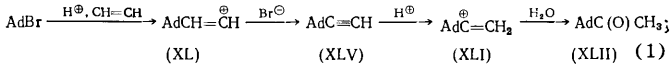
In concentrated sulphuric acid the reaction of acetylene with AdBr leads to 1-adamantyl methyl ketone (XLII) (yield 75%),[135] while the reaction with AdOH results in the formation of a mixture of three products: 1-adamantylacetaldehyde (XLIII) (yield 72%), compound (XLII), and 3-methyl-4-homoadamantanone (XLIV).[136,137] In 90% sulphuric acid 1-ethynyladamantane gives rise to a mixture of the ketones (XLII) and (XLIV).[139]

The study of the reaction of AdOH with acetylene in sulphuric and deuterosulphuric acids showed that compound (XLIII) is formed via the mechanism[138]

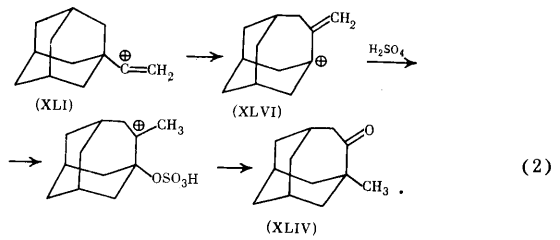


The mechanism of the formation of the ketones (XLII) and (XLIV) has still not been rigorously demonstrated. 1-Adamantyl methyl ketone is probably formed by reaction (1),[137]

while 3-methyl-4-homoadamantanone results from the rearrangement of the adamantanylvinyl cation to the more stable cation (XLVI) [reaction (2)]:[136]



(1)

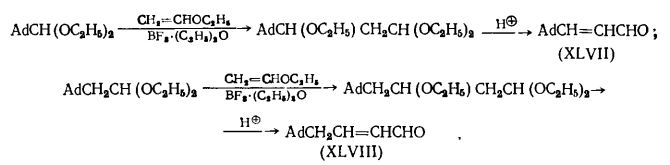


(2)

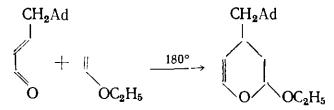
When 1-bromoadamantane was allowed to react with acetylene in solution in methylene chloride in the presence of $AlBr_3$, 1-(1-adamantyl)-2-bromo(chloro)ethylene was formed, which has also been attributed to the intermediate formation of the cation (XLI). It may be that there is also a radical interaction in this instance. 1-Adamantanol does not enter into this reaction[140].

Together with the unsaturated adamantane derivatives discussed above, adamantane-containing unsaturated aldehydes, ketones, acids, and esters have now been also invstigated fairly completely[120].

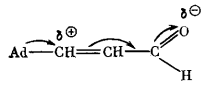
β-(1-Adamantyl)acrolein (XLVII) and γ-(1-adamantyl)-crotonaldehyde (XLVIII) have been obtained from the corresponding diethyl acetals in yields of 84 and 87% respectively[141,142]:



γ-(1-Adamantyl)crotonaldehyde undergoes the Diels–Alder reaction with ethyl vinyl ether to form a substituted 3,4-dihydro-1,2-pyran (XLIX) in 75% yield. On the other hand, the corresponding pyran could not be obtained from compound (XLVII).[141,143]

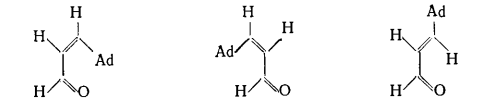


The different behaviour of the aldehydes (XLVII) and (XLVIII) in the reactions with ethyl vinyl ether is probably a consequence of the different degrees of influence of the Ad and $AdCH_2$ residues on the charge separation in the reaction centre of the aldehyde molecule[141]. In compound (XLVII) the electron-donating effect of the adamantyl residue diminishes the positive charge on the α-carbon atom of the aldehyde, as a result of which the molecule is insufficiently polarised for interaction with ethyl vinyl ether:



The methylene group in compound (XLVIII), which is located between the adamantyl group and the β-carbon atom, weakens the effect of the adamantyl residue and the molecule is polarised to a much greater extent.

Another factor which has a significant influence on the ability of the unsaturated aldehydes to undergo the Diels–Alder reaction with vinyl ethers is the configuration of the heterodiene. Heterodienes with the cisoid *trans*-conformation (C) are capable of undergoing this reaction:



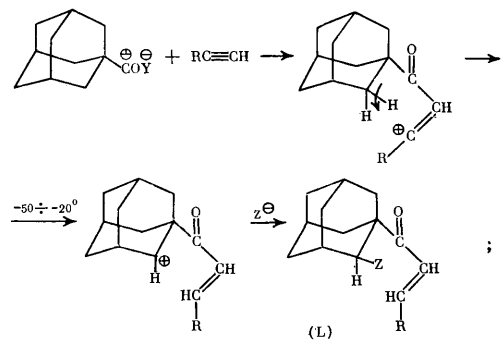
It has been established by infrared spectroscopy[141] that compound (XLVII) exists predominantly in the *cis*-conformation (A), while its homologue (XLVIII) has mainly the conformation (B). The (A) → (B) transition is apparently impossible for compound (XLVII) because of steric hindrance, while the (B) → (C) transition is entirely feasible for compound (XLVIII).[120,141]

The behaviour of 1-adamantyl vinyl ketone[144] in this reaction has also been investigated[141,143].

Under the influence of acid catalysts (formic acid, toluene-*p*-sulphonic acid, hydrochloric acid, and phosphorus pentoxide), 2-ethynyl-2-hydroxyladamantane is smoothly converted into adamantylideneacetaldehyde[145], which readily undergoes various reactions characteristic of aldehydes (the Knoevenagel and Wittig reactions), forming adamantane derivatives which are otherwise difficult to obtain.

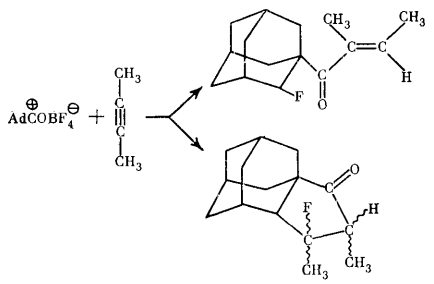
Many adamantane derivatives containing a double bond and a functional group in the side chain have been obtained from the products of the interaction of 1-adamantyl methyl ketone with bromoacetic ester in THF; their reactions have been investigated in two studies[144,146].

The acylation of terminal acetylenes RC≡CH by 1-adamantanoyl tetrafluoroborate or hexafluoroantimonate leads to α,β-unsaturated ketones (L):[147]



The reaction of $CH_3C{\equiv}CH$ and 1-adamantanoyl hexafluoroantimonate in a CH_2Cl_2–$C_2H_4Cl_2$ mixture results in the formaformation mainly of 2-Cl-(*trans*-$CH_3CH{=}CHCO$)Ad.[147,148] 2-Phenyl-1-adamantyl 1-propenyl ketone or 1′-propenyl 2-tolyl-1-adamantyl ketone (L, Z = C_6H_5 or $CH_3C_6H_4$, R = CH_3) and 1-adamantyl 2-phenylpropenyl ketone or 1-adamantyl 2-tolylpropenyl ketone are formed under these conditions in benzene and toluene. The interaction of 1-adamantanoyl tetrafluoroborate and $CH_3C{\equiv}CCH_3$ leads to a mixture of

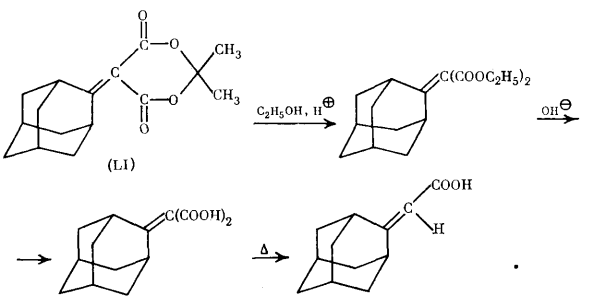
2-fluoro-1-(*cis*-$CH_3CH{=}CHCH_3CO$)Ad and 5-fluoro-5,6-dimethyltetracyclo[6.3.1.1^{3,10}.0^{4,8}]-7-tridecanone:



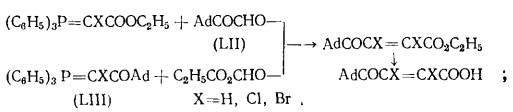
Among unsaturated acids of the adamantane series, adamantylideneacetic[149,150], adamantylidenemalonic[151–153], adamantylidenecyanoacetic[151], β-(1-adamantyl)acrylic[154,155], and α-(2-adamantylacrylic acids[155] are known.

The condensation of 2-adamantanone with malonic acid derivatives (cyanoacetic acid and its methyl ester) makes it possible to obtain derivatives of adamantylidenemalonic acid[151].

The adamantylidene derivative of Meldrum's acid (LI) has been obtained by the reaction of 2-adamantanone with Meldrum's acid in pyridine; 2-adamantylidenemalonic ester has been obtained by the transesterification of compound (LI) in the presence of acid[152]. Hydrolysis of the ester yields adamantylidenemalonic acid, which is converted into adamantylideneacetic acid on decarboxylation:

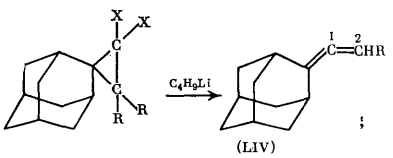


β-(1-Adamantanoyl)acrylic acid and its halogeno-derivatives have been investigated; their esters have been synthesised by the Wittig reaction from 1-adamantylglyoxal (LII) and ethoxycarbonylmethylenetriphenylphosphorane or from ethyl glyoxalate and 1-adamantanoylmethylenetriphenylphosphorane (LIII):[156–159]



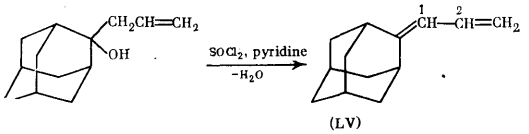
The bromination of β-(1-adamantyl)-β-hydroxybutyric and a series of its derivatives with liquid bromine results in the formation of 2-(1-adamantyl)-1-bromo-2-bromomethylpropiolactone[160].

Functional derivatives of adamantane can be used for the synthesis of compounds containing several double bonds in the side chain. Vinylideneadamantane (LIVa) has been obtained by treating 2,2-dibromo- or 2,2-dichloro-(2-adamantyl)-spiro-1-cyclopropane with butyl-lithium:

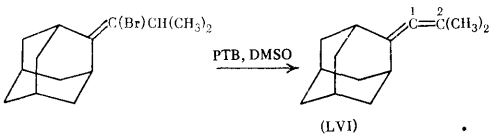


(a) R = H, (b) R = CH_3, (c) R = C_6H_5; X = Cl, Br .

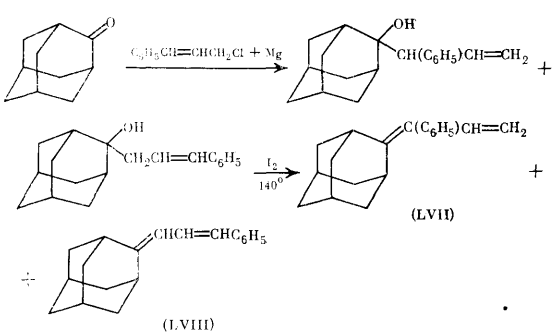
1-Propenylideneadamantane (LIVb) and 2-phenylethynylideneadamantane (LIVc) have been synthesised analogously[63]: the dehydration of 2-allyl-2-adamantanol leads to allylideneadamantane (LV):[161]



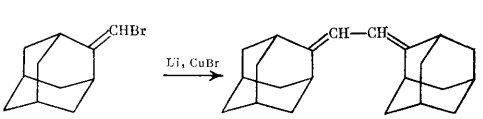
1-(2-Adamantylidene)-2-methyl-1-propene (LVI) has been obtained using potassium t-butoxide (PTB) in dimethyl sulphoxide as the dehydrobrominating agent[63]:



The products of the reaction of 2-adamantanone with 3-chloro-1-phenyl-1-propene and magnesium give rise to a mixture of adamantylidene-2-propenes (LVII) and (LVIII) after dehydration[63]:



1,2-Diadamantylidene-ethane has been obtained by treating bromomethyleneadamantane with lithium in the presence of CuBr:[63]



Certain characteristic features of the variation of the reactivity of the double bond as a function of the size of the substituent, the degree of substitution, and the distance between the double bonds and the nucleus have been discovered in the reaction of dihalogenocarbenes with allenes of the adamantane series[63]. The reactivities of the C(1)=C(2) double bond of vinylideneadamantane (2-Ad=$\overset{1}{C}=\overset{2}{C}H_2$), which is closest to the nucleus, is 12 times lower than in vinylidenecyclohexane and 1.8 times lower than in 1,1-dimethylallene. The cause of this consists in its steric shielding by the adamantane nucleus. The reactivity of the

C(1)=C(2) bond of 1-propenylideneadamantane, which is closest to the nucleus, is smaller almost by a factor of 2 compared with compound (LIVa), while the reactivity of the corresponding bond in methylpropenylideneadamantane (LVI) is zero. Evidently such decrease of reactivity can be accounted for by the steric interaction between the carbene and the methyl group at the C(2) atom in the transition state. In vinylideneadamantane the approach of the carbene to the plane of the C(1)=C(2) bond is equally probable from either side, while in 1-propenylideneadamantane one of the pathways followed in the approach is eclipsed by the methyl group and in compound (LVI) the methyl substituents shield the C(1)=C(2) bond from either side.

The reactivity of the terminal C(2)=C(3) bond in allylideneadamantane (LV) is lower amost by a factor of 6 than in buta-1,3-diene and is higher by a factor of 20 than the reactivity of the double bond in methyleneadamantane (XI, R=R′=H). The reactivity of the 2-Ad=C(1) bond of the diene (LV) is lower by a factor of 36 than the reactivity of the C(2)=C(3) bond. The main cause of the different reactivities of the double bonds in allylideneadamantane is apparently, as in the case of vinylideneadamantane, the steric influence of the adamantane nucleus shielding the 2-Ad=C(1) bond adjoining it. On the other hand, the reduction of the reactivity of the 2-Ad=C(1) bond in allylideneadamantane by a factor of 1.8 compared with methyleneadamantane shows that the steric factor does not operate alone in the case of the diene (LV). As a result of the polarisation of the molecule, the electron-donating effect of the adamantane substituent is transmitted to the terminal double bond and activates it, while the 2-Ad=C(1) bond closest to the nucleus is relatively deactivated. Thus the adamantane nucleus has a strong steric influence on the C=C bond adjoining it, shielding it and hindering the approach of a carbene to it.

1-Adamantyl-substituted allenes, namely 1-(1-adamantyl)-3-chloroallene [162] and 1,3-di(1-adamantylallene [163] have been described:

$$AdCHOHC{\equiv}CH \xrightarrow{SOCl_2} AdCH{=}C{=}CHCl\ ;$$

$$AdC{\equiv}CLi + AdCHO \rightarrow AdC{\equiv}CCHOHAd \xrightarrow{LiAlH_4} AdCH{=}C{=}CHAd\ .$$

The allenes as a rule polymerise on heating, but under certain conditions dimeric products with a cyclobutane structure can be isolated from 1-(1-adamantyl)-3-chloroallene[162]. The attempt to obtain dimers on heating 1,3-di(1-adamantyl)allene was unsuccessful; the reaction mass contained only polymeric products[163].

Allene derivatives of adamantane (LIX) have been obtained by the reaction of alkenynes with AdBr in the presence of metallic lithium[164]:

$$RC{\equiv}CC(R'){=}CH_2 \xrightarrow{Li,\ THF} Li^{\oplus},$$

$$\overset{\ominus}{R}C{=}C{=}C(R')\dot{C}H_2 \xrightarrow{(AdBr)^{\ominus},\ Li} Li^{\oplus},$$

$$\overset{\ominus}{R}C{=}C{=}C(R')CH_2Ad \xrightarrow{H_2O} RCH{=}C{=}C(R')CH_2Ad\ ;$$

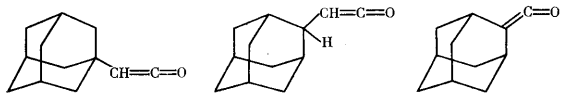
$$R{=}C_2H_5,\ R'{=}H;\ R{=}C(CH_3)_3,\ R'{=}H;\ R{=}R'{=}CH_3\ .$$

1-Adamantylallene has been synthesised by treating 1-chloroadamantane with trimethylpropargylsilane[106,107]:

$$AdCl + CH{=}CCH_2Si(CH_3)_3 \rightarrow AdCH{=}C{=}CH_2\ .$$

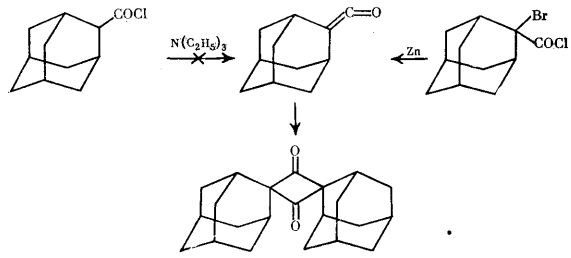
Chloroallene can be obtained with retention of configuration by treating the pure isomer of 2-ethynyl-2,5-dihydroxyadamantane with thionylchloride[133].

Ketens of the adamantane series have also been investigated:

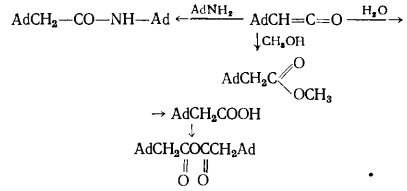


(LX) (LXI) (LXII)

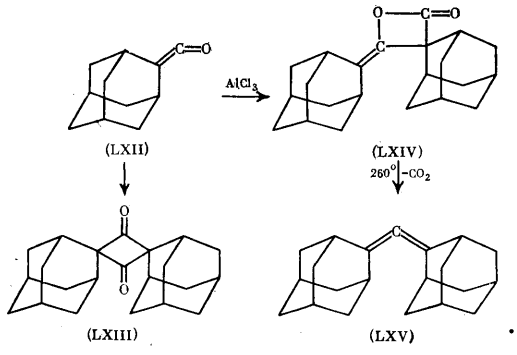
Although the yield of $N(C_2H_5)_3.HCl$ was 90% on treating the chlorides of the corresponding acids with triethylamine, the ketens (LX) and (LXI) could not be obtained in a pure form; only the di-, tri-, and tetrameric products were isolated[72]. The keten (LXII) is formed only when the chloride of 2-bromoadamantane-2-carboxylic acid is treated with zinc in boiling ether, whereupon it is converted immediately into a dimer[72]:



The chemical properties of 1-(1-adamantyl)keten (LX) could be investigated by employing dilute ethereal solutions[72]:



It was shown above that, whereas the keten (LXII) dimerises to the corresponding cyclobutane-1,3-dione under the usual conditions, after the addition of $AlCl_3$ to a boiling dilute ethereal solution of the keten dimerisation to the lactone (LXIV) takes place; on pyrolysis, the compound loses CO_2 and is converted into the allene (LXV):[165]



(LXII) (LXIV) (LXIII) (LXV)

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Thus, apart from the features which it has in common with the chemistry of unsaturated derivatives of other alicyclic hydrocarbons, the chemistry of unsaturated adamantane derivatives is characterised by a series of features determined primarily by the presence of the bulky adamantane

nucleus. As a result of the rigidity of the adamantane structure, dehydroadamantanes are highly strained reactive hydrocarbons, which make it possible to obtain from them a wide variety of mono- and di-substituted adamantane derivatives in one stage.

The reactivity of the compounds containing an exocyclic double bond is appreciably lower as a result of steric shielding; at the same time these compounds are of interest in view of the possibility of obtaining stable complexes. In derivatives with a C=C bond in the α,β-position in a side chain, the bond is subjected to appreciable shielding and an electron-donating influence by the adamantyl group. These compounds are also extremely reactive, undergo homopolymerisation and particularly copolymerisation reactions, and can be used to prepare polymeric materials with valuable properties as well as various functional derivatives of adamantane which are of interest from the standpoint of their biological activity.

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Kinetics and Mechanism of the Oxidation of Polymers in a Stressed State

N.Ya.Rapoport and G.E.Zaikov

The characteristics of the kinetics and mechanism of the chain oxidation of stressed polymers are considered as a result of structural and conformational changes occurring in polymer matrices under the influence of mechanical stresses. Attention has been concentrated on the kinetics of the autoxidation of polyolefins subjected to the influence of stretching stresses and the kinetics of the ozonisation and autoxidation of stressed raw and cured rubbers. The results of studies on the kinetics of individual stages of the chain process, namely initiation, propagation, degenerate branching, and termination of kinetic chains in stressed polyolefins, are surveyed; the effects of orientational stretching in the kinetics of the oxidation of polyolefins are considered. The relation between the kinetics of oxidation, durability, and the mechanism of the decomposition of oriented specimens subjected to an external mechanical load is discussed. The method of defectoscopy of polymers subjected to the simultaneous influence of mechanical stresses and an oxidising medium, based on the local character of the oxidation of stressed polymers, is considered.
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I. INTRODUCTION

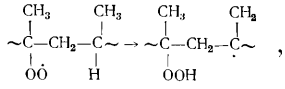
The use of polymeric materials as a rule involves the operation of mechanical stresses applied either from the outside or internal stresses arising during the conversion of the polymer into a finished article and also in the course of the ageing of the polymer. Chemical reactions leading to the ageing of polymers therefore usually take place in stressed polymer matrices. A characteristic feature of chemical reactions in solid polymers is a relation between the reaction kinetics and the structural-physical parameters of the matrix, which differ significantly for the unstressed and stressed specimens. The task of predicting the durability of polymeric articles and the search for the optimal ways of stabilising polymers require the knowledge of and allowance for the influence of mechanical stresses on the kinetics and mechanism of ageing processes. Since the publication of the first study in which the accelerating influence of mechanical stresses on the rate of oxidation of vulcanised rubbers was demonstrated (the authors called this phenomenon mechanical activation[1,2]), more than 30 years have elapsed and extensive and varied experimental data concerning the influence of mechanical stresses on the kinetics of the oxidation of polymers of different classes by molecular oxygen and ozone have accumulated. In the present review an attempt is made to analyse and survey these data.

The structural microheterogeneity of solid polymers, even those in the amorphous state (see, for example, Jech[3] and Arzhakov et al.[4] as well as Lebedev's review[5]) has important kinetic consequences.

1. The microheterogeneity of the distribution of the reactants in the matrix leads to the possibility that their local concentrations differ significantly from the average values and the experimental rate constants calculated in relation to the average concentrations differ appreciably from the true values. The microheterogeneity in the distribution of the reactants can also be one of the causes of the manifestation of polychromatic kinetics characteristic of reactions in solid matrices: the reactions take place at a higher rate in regions with higher local concentrations and, as these regions become exhausted, those with lower local concentrations are "manifested". Formally, this will be described as a distribution with respect to the reaction rate constants. The microheterogeneity of the distribution of reactants is shown most distinctly in amorphous-crystalline polymers. For example, a stable nitroxy-radical is localised exclusively in the amorphous phase of polypropylene (PP)[6]. Antioxidants are also localised in the amorphous regions and the solubility of antioxidants in isotropic PP depends on its supermolecular structure: 80% of antioxidants are dissolved within spherulites and in the interfibril and defective intrafibril regions, while 20% are localised at the interspherulite interfaces[7]. Allowance for the heterogeneity of the distribution of antioxidant molecules in the polymer matrix is extremely important for the practical stabilisation of polymers.

2. The most important structural-physical parameter of a solid polymer for kinetics is the distribution with respect to the frequencies and amplitudes of molecular movements, which also leads to a distribution with respect to the reaction rate constants. This problem has been analysed in detail in a review[8]. The relation between the kinetics and molecular mobility is determined, firstly, by the dependence of the rate of diffusional encounters between the reactant molecules on the molecular mobility of the polymer, and, secondly, by the influence of the molecular dynamics directly on the chemical reactions step (see, for example, Girva and co-workers[6,9,10]). The possible physical mechanisms of the influence of molecular mobility on the reactivity have been discussed[8].

3. Finally the relation between the reaction kinetics and the set of polymer conformations, specific to reactions in polymer matrices, is due to the fact that many reactions in polymers take place intramolecularly. An example may be provided by the radical substitution reaction



(I)

which is a reaction involving the propagation of kinetic chains in the chain oxidation of polyolefins, leading to the migration of a free valence in the specimen. The ratio of the rate constants for the intramolecular and intermolecular reactions (I) in 2,4-dimethylpentane, a low-molecular-weight

analogue of polypropylene, at 100 °C is approximately two orders of magnitude[11]. An important structural requirement for the intramolecular transfer of a hydrogen atom from a carbon atom to a peroxy-radical is the formation of six-membered (or larger) rings in the transition state. In general, the abstraction of a hydrogen atom by a free radical requires that the bond ruptured should be located on the axis of the unpaired electron at a distance of 1.5–2 Å from the latter, i.e. that the pre-start state of the reactant should be located on the reaction coordinate[8]. Evidently the probability of the appearance of such a pre-start state and the probability of the formation of a transition complex having the optimum structure depend on the local conformation of the reaction centre. In polymers structural relaxation takes place slowly and the local mobility of a section of the macromolecule depends on its local conformation[12], so that one can expect a dependence of the kinetics of intramolecular reactions on the set of conformations of the polymer. Examples of such a relation will be considered below.

The conformations of macromolecules can influence, albeit to a smaller extent, also the rates of intermolecular reactions; for example, the rate constant for the abstraction of a hydrogen atom by the t-butoxy-radical in atactic PP at 45 °C is lower by a factor of two than in 2,2,4-trimethylpentane[13], which is associated with the steric hindrance to the reaction in the polymer; such hindrance should depend on the conformations of the macromolecules.

Under the influence of mechanical stresses, all the structural-physical parameters of the matrix significant for the kinetics of chemical reactions change in polymers. We shall consider mainly the effect of stretching stresses, which has been studied in greatest detail.

In the first place we shall note that two types of elasticity—predominantly entropic and predominantly energetic—are characteristic of polymers as a medium consisting of long and flexible chain molecules. The appearance in the polymer of entropic stresses is associated with the deviation of the conformations of the macromolecules from the statistically most probable conformations†. Energetic stresses are determined by the distortion of the valence angles and by the change in the lengths of the chemical bonds.

The calculated moduli of elasticity for various types of deformation of macromolecules have been published[14]. For the "pure" extension of a C=C bond, the modulus of elasticity is 740 GPa, for the extension of a "zig-zag" chain it is 180–340 GPa, and for the bending of a C=C bond and the hindered rotation of helices the moduli are 80 and 4–7 GPa respectively. The moduli of elasticity corresponding to the entropic and energetic stresses differ by two orders of magnitude. The deformation of polymers under the influence of external stretching stresses therefore initially takes place as a result of conformational rearrangements, which lead to the appearance of internal entropic stresses, and only after their completion does the distortion of valence angles and bonds, leading to the weakening of chemical bonds in the macromolecular skeleton, begin.

As will be shown below, entropic stresses become fixed ("frozen") in the amorphous phase of oriented amorphous-crystalline polymers if the latter are not subjected to a special heat treatment inducing the relaxation of the stress (annealing). Energetic stresses in amorphous-crystalline polymers arise after the application of an additional external load to oriented specimens, particularly in the region of plastic deformations.

† As a consequence of the presence of barriers to internal rotation, a purely entropic elasticity does not exist in polymers just as an ideal gas does not exist. We are only concerned with the question which component of elastic forces—entropic or energetic—is dominant.

II. THE INFLUENCE OF MECHANICAL STRETCHING STRESSES ON THE STRUCTURAL-PHYSICAL PARAMETERS OF POLYMER MATRICES

1. The Change in the Supermolecular Structure of Polymers under the Influence of a Stretching Load

Under the influence of stretching stresses, high and reversible (in the case of rubbers) deformations develop in amorphous highly elastic polymers (raw and cured rubbers) and the macromolecules are subjected to an orientation, which relaxes after the removal of the load (the preferred directions in the disposition of the macromolecular axes relative to the stretching axis appear). An enforced elasticity is manifested in vitreous amorphous polymers and an orientation arises which persists after the removal of the load at temperatures not exceeding the glass point. In isotropic amorphous-crystalline polymers the stretching stresses lead to profound structural rearrangements; the spherulitic structure is transformed into a fibrillar structure.

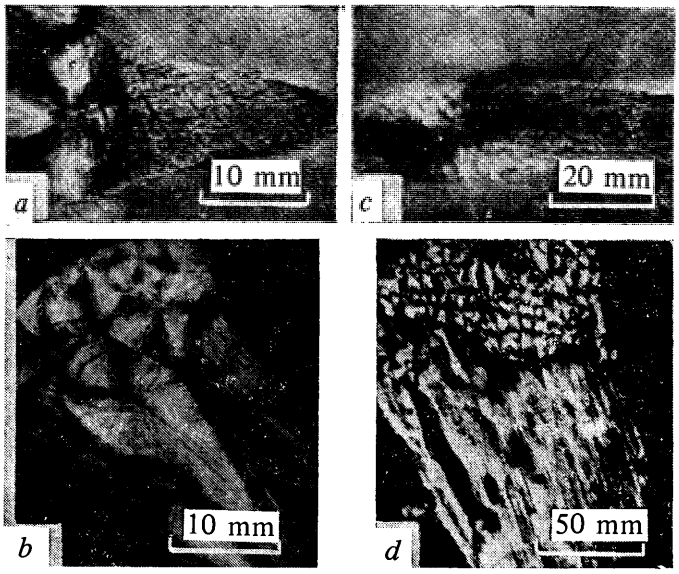


Figure 1. Stages in the deformation of a spherulite and the structure of the neck in isotactic PS[15].

The photomicrographs in Fig. 1 illustrate different stages in the deformation of a single spherulite in isotactic polystyrene (PS)[15]. The deformation of the spherulite takes place abruptly with formation of a "microneck" and a distinct interface persists between the deformed and undeformed parts of the spherulite. After the conversion of the entire spherulite into the "microneck", uniform deformation of the resulting oriented structure takes place and the formation of the microfibrillar structure is completed. In contrast to the

spherulitic structure, the microfibrillar structure is characterised by a distinct anisotropy of its properties. The microfibrils distributed along the direction of the extension contain alternating regions with crystalline and amorphous orders whose dimensions depend on the stretching (and annealing) conditions. The linkages between individual crystallites within the fibrils are formed by "crossing" macromolecules and also by a network of engagements between macromolecules, each of which returns to its "own" crystallite. In the transverse direction the individual microfibrils are linked by cohesive forces and crossing chains whose number is significantly lower than in the intrafibril regions. The transverse strength of monoaxially oriented polymer specimens is therefore much lower than their longitudinal strength.

As a result of the structural rearrangements induced by mechanical stresses, the proportions of the low-molecular-weight compounds in polymers and their solubilities change and there is a significant alteration of the molecular-dynamic properties of the matrices and the set of their conformations.

2. The Change in the Solubilities of Low-Molecular-Weight Compounds in Stressed Polymers

For elastomers, this question has been discussed in greatest detail[16] for rubbers stressed in a complex manner. Under the conditions of static compression, mechanical stresses lead to an anomalous transport of low-molecular-weight substances (plasticisers and inhibitors). The situation is different when elastomers are acted upon by stretching stresses: for deformations which do not induce the crystallisation of raw rubber (less than 200%), the permeability and diffusion characteristics hardly change[17,18]; for greater deformations, the crystallisation of raw rubber results in a significant decrease of the sorption and diffusion coefficients of low-molecular-weight compounds[17].

For vitreous amorphous and amorphous-crystalline polymers, the dependence of the permeability parameters on the stretching stress is complex[19–23]. In the region of stresses corresponding to the elastic deformations of the polymer, the degree of sorption of low-molecular-weight substances increases with increase of the stress owing to the increased fraction of the free volume in the specimen (in the majority of amorphous-crystalline polymers the Poisson coefficient is less than 0.5). In the region of stresses corresponding to plastic deformations, the sorption of low-molecular-weight compounds decreases appreciably with increase of deformation as a consequence of the decreasing density of the amorphous component[21]. The authors[21] based their interpretation of the experimental results on the model of impermeable microfibrils distributed in the bulk of the interfibrillar amorphous component. Despite the approximate nature of this model, in most cases its application is justified by the fact that the solubilities of low-molecular-weight compounds in amorphous-crystalline polymers are proportional to the fraction of the amorphous phase[24,25].

The study of the influence of mechanical stresses on the permeability parameters for oxygen is naturally of greatest interest for the elucidation of the kinetics of oxidation processes. There are few such data in the literature. It has been shown[25] that the solubility of oxygen in PP is proportional to the fraction of the amorphous phase and depends on the supermolecular structure of the polymer. However, one should note that the concept of the impermeability of the crystalline phase of amorphous-crystalline polymers to oxygen is not entirely correct. For example, in the radiation-induced initiation of radicals in the crystalline phase of PP in an oxygen atmosphere, all the alkyl radicals are converted into peroxy-radicals, i.e. oxygen diffuses into the crystalline phase of the PP (and into the even looser crystalline phase of poly-4-methylpent-1-ene). This is not observed in polyethylene (PE): the dense crystalline regions of this polymer are impermeable to oxygen[24] (for further details, see the relevant review[26]—pp.22–30). The solubilities of oxygen in unannealed (subjected to an entropic stress) and annealed (unstressed) oriented films of isotactic PP have been compared[27]. The solubility in the unstressed oriented films proved to be higher by a factor of 1.5–2.5 than in the annealed films. However, the influence of mechanical stresses on the sorption characteristics of the polymer is significantly weaker than their influence on the molecular-dynamic and diffusion parameters.

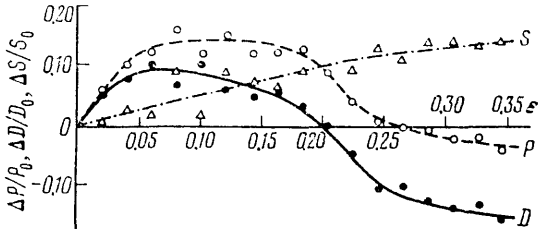


Figure 2. The relative changes in the sorption (S), diffusion (D), and permeability (P) coefficients for CO_2 in PE films as a function of the degree of deformation ε of an isotropic film[21].

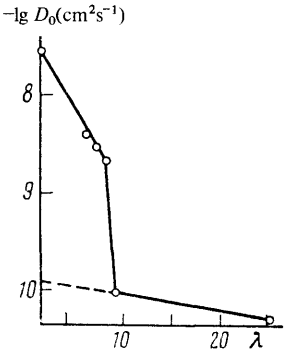


Figure 3. Variation of the diffusion coefficient of CH_2Cl_2 in PE with the degree of orientational extension λ.[21]

3. The Changes in the Molecular Dynamics and Diffusion Parameters in Oriented and Stressed Polymers.

The deformation of elastomers (in the absence of crystallisation) does not change appreciably their diffusion characteristics[17], while the diffusion characteristics of amorphous-crystalline polymers can change by several orders of magnitude on deformation. In the region of small reversible elastic deformations of PE (Fig.2), the diffusion coefficients of gases increase somewhat (like the increase in the degree of

sorption, this is also evidently associated with the increase in free volume), but, after the appearance of the plastic component of the deformation, the diffusion coefficient falls sharply (Figs.2 and 3)[21]; for example, threefold orientation stretching of PE leads to a decrease of the diffusion coefficient of gases by a factor of 40–50. The most marked diminution of the diffusion coefficient takes place over a narrow range of degrees of stretching apparently corresponding to the termination of the formation of a microfibrillar structure[21]. An analogous dependence on the degree of stretching has been observed for the diffusion coefficients of nitrogen and methane in oriented PP (Fig.4)[28].

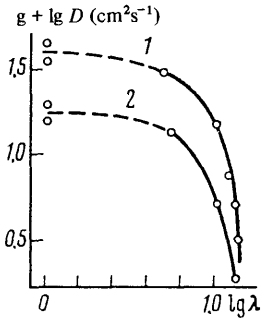


Figure 4. Variation of the diffusion coefficients of nitrogen (curve *1*) and methane (curve *2*) in PP with the degree of extension λ.[28]

One should note that the influence of the deformation of the polymer on the diffusion coefficients of low-molecular-weight substances is greater the greater the size of the diffusant molecule[20].

The change in the polymer permeability parameters on orientational extension is associated with the presence of unstressed extended fragments of the micromolecules in the amorphous phase. The more complete was the preceding relaxation of the amorphous phase, the smaller were the changes in the sorption and diffusion coefficients for the same degree of extension; an increase of the extension temperature or annealing of the oriented polymer above the extension temperature therefore diminish appreciably the changes in the permeability parameters[21].

The changes in the translational diffusion coefficient of low-molecular-weight substances in stressed oriented polymers, apart from the molecular-dynamic polymers, have purely geometrical causes: during their migration, the species must move round impermeable or relatively impermeable crystallites (or microfibrils), which leads to an increase in the length of the diffusional transport path. The contribution of the purely geometrical causes to the change in the translational diffusion coefficients on deformation of the polymer can be isolated by the paramagnetic probe method. The influence of the degree of extension of PP on the rotational and translational mobility of a stable nitroxy-radical, namely the 2,2,6,6-tetramethylpiperidin-1-oxy-radical, has been investigated[29].

Data for the dependence of the translational and rotational diffusion coefficients of this radical in PP on the degree of extension at 80° and 130 °C are presented in Table 1. Evidently at 80 °C, where $\lambda = 7$, the translational diffusion coefficient in the specimen decreases by a factor of 8 compared with the isotropic polymer, while the rotational diffusion coefficient diminishes less than by a factor of 2. These data refer to specimens in which the probe radical has been introduced before extension; on the other hand, if the radical is introduced into specimens which have already been oriented, then, up to $\lambda = 7$, the rotational frequencies do not change at all relative to the isotropic polymer, since the radical enters the "softest" and accessible regions of the specimen. Nevertheless the translational diffusion coefficient of the radical falls compared with its value in the isotropic polymer, which is evidently due solely to geometrical obstacles, which increase as the polymer is oriented. The data obtained made it possible to estimate the coefficient γ, which takes into account the increase, due to the geometrical obstacles arising in the orientational extension, of the path traversed by the radical: $\gamma = 1.4$ and 2.1 for specimens with $\lambda = 4.5$ and 7 respectively. Consequently, for specimens with $\lambda = 7$, all the changes in the translational diffusion coefficient greater than by a factor of two are due to the decrease of the segmental mobility of the macromolecules.

Table 1. Dependence of the translational (D_t) and rotational (D_r) diffusion coefficients of the probe radical on the degree of extension of PP at 80° and 130 °C.[29]

λ	$10^9 D_t$, $cm^2 s^{-1}$	$10^{-8} D_r$, s^{-1}	$10^7 D_t$, $cm^2 s^{-1}$	$10^{-9} D_r$, s^{-1}
	80° C		130° C	
0	5.4	7.9	2.9	7.2
4.5	1.9	6.6	1.7	4.7
7.0	0.7	4.6	1.9	2.8
10.0	—	4.3	—	2.0

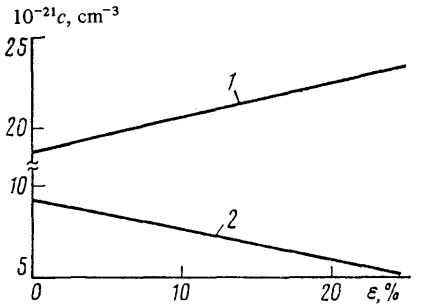


Figure 5. Variation of the concentrations of the *trans*-conformation (line *1*) and the *gauche*-conformation (line *2*) in oriented PE ($\lambda = 10$) under the conditions of additional deformation along the stretching axis[38].

We may note that at room temperature the rotation of the radical in PP is significantly hindered and is relatively insensitive to the stress[29]. The low sensitivity of the rotational mobility of the radical to the external load applied to PP at room temperature is apparently associated with the same factor[30,31]: the maximum changes in the rotational correlation time of the probe in the range of stresses from 0 to 250 MPa do not exceed 9%. Furthermore, NMR spectroscopy has revealed significant changes in the segmental mobility of the molecules of oriented PP subjected to an external load[32].

4. The Change in the Set of Conformations of Micromolecules under the Influence of a Stretching Load.

The change in the molecular dynamics of polymers, to which a load has been applied and which are subjected to orientation, takes place as a result of a change in the set of conformations: the depletion of the specimen in the mobile coiled conformations and its enrichment in the relatively immobile extended conformations (i.e. a decrease of the entropy of the system)[33-39]. Fig.5 illustrates the changes in the concentrations of the *gauche*- and *trans*-isomers when a load is applied to oriented PE (according to the data of Pakhomov et al.[38]). The dependence of the contents of various conformers in the polymer chain on the degree of its extension has been studied theoretically[39]. It was shown that in the initial stage of the extension the chain is stretched mainly as a result of the reorientation of its elements: the coiled G-isomers are distributed more uniformly along the chain, preferentially in the vicinity of extended T-isomers as neighbours, and the fraction of G-isomers begins to fall appreciably only for fairly high degrees of extension (Table 2). The relative positions of the coiled isomers are characterised by the concentrations of triads containing one *trans*-isomer and two coiled isomers (Fig.5). The most stable triads, containing the G-isomers in the extended chain, are the TGT and GTG′ triads, which is natural, since precisely these triads cause the smallest shortening of the chain for the given number of G-isomers (they are incorporated in a "kink" in the PE chain). It has been shown experimentally[38] that, in the region of elastic deformations of PE, the extension of amorphous layers from 40 to 60 Å leads to a more than 30% decrease of the number of TGT and GTG′ triads; on further extension, the specimen breaks. It is natural to suppose that the synchronous disappearance of the above triads is associated with the straightening out of the "kink", i.e. with a simultaneous conversion of two G-isomers into T-isomers; this is also indicated by the activation energy for the deformation (~ 8 kcal mol^{-1}), exceeding by a factor greater than two the height of the barrier to internal rotation in the PE chain.

Table 2.

$\varkappa$	α_{TG}	α_{GG}	α_{G}
0	0.94	0.68	0.80
1	0.90	0.70	0.81
2	0.86	0.72	0.82

Note. α are the degrees of extension of the chain for which the concentrations of the isomers and diads containing the G isomers decrease by a factor of two compared with the unstretched chain ($\alpha = 0$) and $\varkappa = E/kT$ is the thermodynamic rigidity of the chain[39].

It has been shown[39] that the decrease of the concentration of the TGT and GTG′ triads begins for fairly high degrees of extension of the chain (~ 0.9). The fact that the number of these conformers diminishes by more than a third in prerupture PE deformations means that the fraction of chains stretched to this extent is more than one third of the total number of crossing chains; the long range of the degrees of deformation (~ 50%) in which the concentration of these triads diminishes enabled the authors[39] to postulate that in some of the chains there is additional stretching of the fully extended *trans*-chains as a result of the deformation of the valence angles.

It must be emphasised that the above investigators[39] based their calculation on the PE chain model in which the conformation extended to the maximum extent consists of a flat zig-zag. As a consequence of the interaction of the methyl groups, the flat zig-zag does not occur in PP and the conformation extended to the maximum of extent consists of a sequence of TGT triads corresponding to the α-helix in PP crystals.

It follows from the above that the statistical weight of the mobile coiled conformations diminishes following the extension of polymer chains. The corresponding calculations have been carried out for the PE chain[40]. From these results, it was possible to estimate the contribution of the entropic elasticity to the forces tending to contract the extended polymer chain. In terms of order of magnitude, these forces are close to the energetic contribution by the elastic forces of the "kink" isomers (associated with the existence of a barrier to internal rotation) but have the opposite sign.

The variation of the free energy F of the partly extended chain as a function of the distance between its ends is illustrated in Fig.6[14] (p.129). The minimum free energy of the chain corresponds to a distance between its ends $r = (n-n_k)\sqrt{2}/3a$, where n is the total number of C–C bonds, n_k is the number of "kink" isomers, and a is the length of the C–C bond. If the ends of the chain are displaced from the equilibrium positions, then elastic forces arise which are associated with the hindered rotation of the *gauche*-bonds outside the plane of the zig-zag of the PE chain and the deformation of the *trans*-bonds in the plane of the zig-zag.

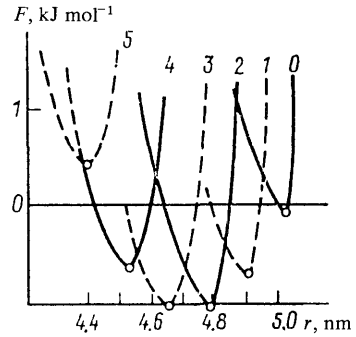


Figure 6. Variation of the free energy F of a partly extended PE chain with the distance r between its ends; the numerals against the curves represent the numbers of kink isomers[14] (p.129).

The modulus of the chain containing different conformers is specified by the expression

$$1/\bar{E} = \sum_i x_i/E_i ,$$

where E_i are the moduli of the individual conformers and x_i are their volume fractions. The smaller the content of *gauche*-conformers in the chain the greater the rigidity of the latter; the presence of only five "kink" isomers in the PE chain reduces the modulus from 200 to 9.5 GPa. It is seen from Fig.6 that, when the chain is extended, there are transitions between individual conformational states and the transition to the more extended conformation removes the axial stress from the section of the chain considered, i.e. it is a thermodynamically favourable process.

The results of a calculation by Darinskii and Neelov[39] and Pechhold[40] are extremely important for the interpretation of the experimental data obtained in the study of the kinetics of the oxidation of oriented and stressed polyolefins.

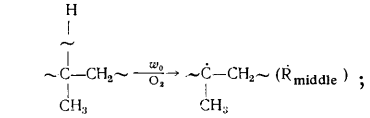
III. KINETICS AND MECHANISM OF THE OXIDATION OF STRESSED POLYMERS.

The discovery in 1950 by Kuz'minskii and co-workers of the phenomenon of the mechanical activation of the oxidation of raw and cured rubbers[1,2,41], the wisely familiar acceleration of the ozone-induced cracking of resins under a mechanical stress (see, for example, Refs.42–53), and the acceleration of the degradation of the C–C bonds in the macromolecular skeleton of mechanically stressed polymers[54] led to the idea that the oxidation reaction is as a rule accelerated under the influence of mechanical stresses. The onset of the breakdown of these traditional ideas dates back to the middle 1970's when studies on different polymeric objects and by different methods, showing that the acceleration of chemical reactions and particularly the oxidation reactions under the influence of mechanical stresses is by no means a universal phenomenon, were published independently and almost simultaneously[55–68]. This is associated with the fact that oxidation is usually a complex chain process whose individual stages vary differently in the stressed polymer. We shall consider the influence of mechanical stresses (1) on the kinetics of the oxidation of polyolefins under the influence of molecular oxygen and ozone and (2) on the kinetics of the ozonisation and oxidation of raw and cured rubbers.

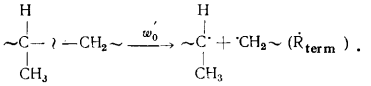
1. Kinetics and Mechanism of the Thermo-oxidation of Stressed Polyolefins under the Influence of Molecular Oxygen

The generally accepted mechanism of the chain oxidation of polyolefins is presented below.

Initiation:



(0)

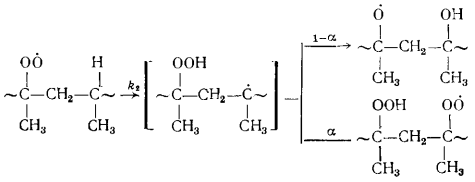


(0′)*

Chain propagation:

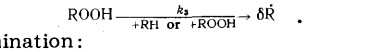


(1)



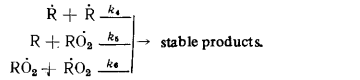
(2)*

Branching:



(3)*

Chain termination:



(4)
(5)
(6)

The asterisk denotes stages in which polymer chains may be degraded. The mechanism includes four main stages: initiation, propagation, degenerate branching, and termination of kinetic chains. The changes in the overall kinetics of the oxidation in stressed polyolefins occur as a result of the influence of mechanical stresses on the rate of each of the above stages. We shall consider in succession the data available at present concerning the influence of stretching stresses on the rate of each stage.

(a) Primary initiation. The primary initiation of radicals in stressed polyolefins can take place via two main pathways: reaction (0)—"direct" interaction of oxygen with macromolecules leading to the rupture of a C–H bond and the formation of internal alkyl macroradicals (this is the "usual" initiation stage in unstressed systems in which various admixtures such as the residues of the polymerisation catalysts apparently play a significant role[69]) and reaction (0′)—the rupture of C–C bonds in the macromolecular skeleton with formation of terminal macroradicals (this reaction proceeds only in stressed polymers).

The influence of structural stresses on the rate of reaction (0)—the rupture of C–H bonds under the influence of various hydrogen acceptors—has been investigated[62,63] for model compounds—unstressed and stressed cyclic paraffins. It has been shown[62] that the reaction of stressed cyclic paraffins with olefin is accelerated relative to the unstressed six-membered ring: by a factor of 48 for the eight-membered ring, by a factor of 89 for the nine-membered ring, and by a factor of 6 for the less stressed twelve-membered ring. An attempt has been made[64] at a quantitative interpretation of these results. The rate constant for the reaction with ozone depends on the excess energy of the ring subjected to stretching stresses, in conformity with the expression

$$\ln (k_i/k_0) = \gamma (E_{\text{exc}}^{\alpha}/RT) \ .$$

The authors[64] suggested that, in any reaction accompanied by the rehybridisation of the sp^3 carbon atom to the sp^2 state and hence by an increase of the valence angle, a stretching stress should reduce the activation energy: the increase of the valence angle under the influence of the stretching stress increases the energy of the molecule in the initial state by $E_{\text{init}} = 0.5C(\Delta\alpha)^2$. where C is a constant and $\Delta\alpha$ the radiation of the valence angle from the optimum value. During the abstraction of a hydrogen atom, the deviation of the angle from the optimum value diminishes and $E^{\neq}$ is therefore lower than E_{init}, which leads to a decrease of E_{act}. The above is valid also for reactions involving the abstraction of a hydrogen atom from polyolefin molecules.

This hypothesis has been tested experimentally[65] for the reaction of ozone with PP, high-density polyethylene (HDPE), and low-density polyethylene (LDPE). It was shown that the rate of accumulation of carbonyl groups in PP and PE increases linearly with increase of the stress. The rate of relaxation of the stress under the conditions of constant deformation differs significantly in oxygen and in ozone, the difference increasing with increasing stress, which indicates an increase of the rate of ozone-induced degradation of the macromolecule as the stress becomes more pronounced.

Studies on the ozone oxidation of the surfaces of isotropic PP films with different thermal histories[66] demonstrated the faster "combustion" of the bonds corresponding to the long-wavelength wing of the 973 cm^{-1} band in the absorption spectrum of PP. The authors interpreted this as a result of the faster reaction with ozone of the most overstressed C–H bonds. However, the long-wavelength wing of the band can correspond to bonds in other conformations rather than the overstressed bonds[70] and the result obtained by

Krisyuk[66] is thus a consequence of the different reactivities of different conformers. At the present time there are insufficient data for the solution of this problem.

The results of the above studies[62,64-66] have been surveyed by Popov et al.,[31] who demonstrated that the orientation and external load applied to oriented specimens have effects of different sign on the rate of the ozone oxidation of PP and PE. It was shown that the observed effects cannot be accounted for by a change in the degree of orientation, the degree of crystallinity, and the molecular dynamics of the polymers under load. Popov et al.[31] concluded that the main cause of the acceleration of the reactions of ozone with PP and PE under load is the stress-induced decrease of the activation energy for the abstraction of a hydrogen atom from the polymer chain. Unfortunately, the investigators[31,65,66] inferred the acceleration of reaction (0) in stressed polymers from the increase of the rate of acceleration of secondary products (carbonyl groups, breaks in macromolecules), which are produced as a result of subsequent reactions of the alkyl macroradicals generated in reaction (0).

However, the author's view[31,65,66] is apparently valid: additional (albeit also indirect) confirmation of the acceleration of reaction (0) in stressed PP has been obtained recently[71] (Fig.7). In the uninhibited oxidation of PP subjected to an external load there is a range of stresses in which the durability of the polymer is determined by the rate of the thermo-oxidative chain degradation and depends only slightly on the load[59,72,73] (Fig.7, curve *1*). In the inhibited specimen the chain oxidation process is suppressed, as a result of which in the region of low stresses its durability increases by more than an order of magnitude compared with the uninhibited specimen and is determined by the inhibitor consumption time, which depends on the rate of initiation (after the consumption of the inhibitor, the oxidative chain degradation leads to rapid decomposition of the specimen).

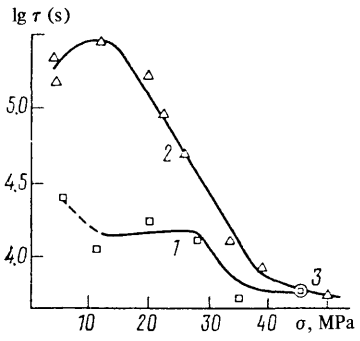


Figure 7. Isotherms of the durability in air of oriented PP ($\lambda = 7$), both uninhibited (curve *1*) and inhibited (curve *2*); inhibitor—Ionox; [InH] = 3×10^{-3} mol kg^{-1}; point *3* corresponds to the durability of the inhibited specimen *in vacuo*[71].

Fig.7 (curve *2*) shows that in the range of stresses 15–35 MPa the durability of the polymer falls exponentially with increase of the applied stress, which may indicate an increase of the rate of initiation [it will be shown below that in the range of stresses indicated the oxidation is initiated via reaction (0)]#. The causes of the increase of the rates of reaction may be associated with the fact that the rehybridisation of a carbon atom from the sp^3 to the sp^2 state as a result of the hydrogen atom abstraction reaction entails an increase in the length of the macromolecular fragment, which promotes the relaxation of part of the stress, and not with the deformation of the valence angles in the pre-start state (the absolute values of the applied stresses are fairly low—see Fig.7).

The second initiation reaction [reaction (0') involving the dissociation of a C–C bond in the macromolecular skeleton], leading to the formation of terminal macroradicals, takes place only in stressed polymers. Its rate increases exponentially with increase of the applied stress, as shown in numerous studies of Zhurkov's Leningrad School (see, for example, Regel' et al.[54]).

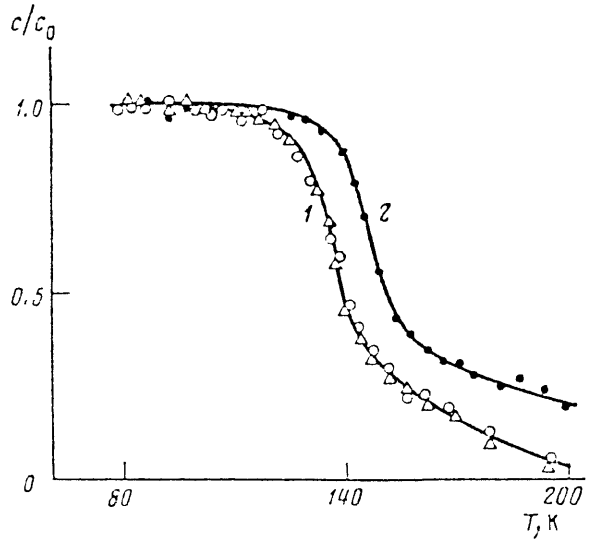


Figure 8. "Heating" curves for the reaction between Ṙ and NO in isotropic PP specimens (curve *1*) and specimens oriented with $\lambda = 9$ (curve *2*).[77]

(b) Propagation of the kinetic chains. The first kinetic chain propagation reaction involves the addition of oxygen to alkyl macroradicals [reaction (1)]. In polymers this reaction proceeds under microdiffusional conditions[74-76] and its rate is controlled by the rate of microdiffusion of oxygen via the polymer matrix. The decrease of the translational mobility of gases in PP as a result of orientational extension (see Fig.4 and Tochin et al.[28]) should lead to a decrease of the rate of reaction (1) in oriented PP. It follows from the data of Yakimchenko et al.[77] that this is indeed observed.

An unambiguous interpretation of these results is hindered by the fact that the oxidation under load is of a distinctly local character (see below): the concentration of the inhibitor in the region of the future break can be partly made good as a result of diffusional "suction" from neighbouring regions where it is consumed more slowly, the translational diffusion coefficient of the antioxidant depending on the applied stress[117].

The above investigators[77] studied the rate of reaction between $\dot{R}$ and NO (modelling the reaction of $\dot{R}$ and O_2) in isotropic and oriented PP. Fig.8 presents the "heating" curve for this reaction in isotropic and oriented ($\lambda = 9$) PP specimens and Fig.9 presents the kinetic curve for the destruction of the radicals $\dot{R}$ at a fixed temperature. Evidently alkyl radicals are destroyed more slowly in oriented PP than in the isotropic polymer. This is consistent with the shift of the spectrum of free energies of activation towards higher values.

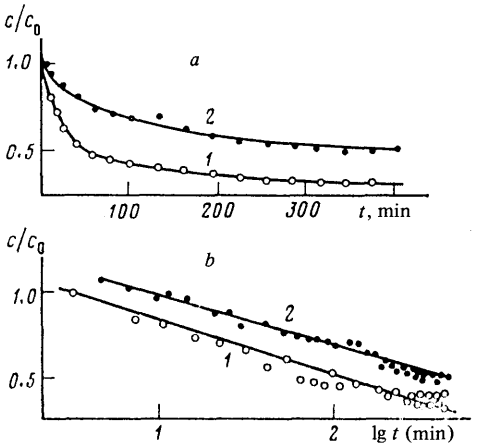


Figure 9. Kinetic curves for the destruction of alkyl radicals by the reaction between $\dot{R}$ and NO in PP (*a*) and the corresponding semilogarithmic plots (*b*)[77]; for legend, see Fig.8.

The application of an additional load to oriented specimens can entail a change in the diffusion coefficients of oxygen relative to the unstressed oriented specimens and the corresponding change in the rate of reaction (1); however, according to Iasuda and Peterlin[20,21], in the region of reversible deformations the scale of these changes is significantly smaller than on transition of the polymer from the isotropic to the oriented state. It may be expected that, in PP specimens maintained under isometric conditions (with the ends fixed), i.e. in the state of elastic deformation at the oxidation temperature (130 °C), the diffusion coefficient of oxygen is somewhat greater than in specimens subjected to shrinkage (for a degree of extension $\lambda = 9$ at 130 °C, the shrinkage is ~ 20%). However, the relevant experimental data are not available in the literature.

The changes in the translational diffusion coefficient of a bulky stable nitroxy-radical (the 4-methyl-2-spiro-cyclohexyl-2,3,3,4-tetrahydrofurano-1,2,3,4-tetrahydroquinoline-nitroxy-radical) in oriented PP subjected to a monoaxial load ($\lambda = 6$) at 120 °C have been investigated[74]. It was observed that, in a certain range of stresses, the diffusion coefficient of the radical increases with increase of the stress and then falls sharply, the difference between the maximum and minimum diffusion coefficients of the radical observed in the investigation amounting to approximately one order of magnitude. We have already mentioned that the influence of the deformation of the polymer on the diffusion coefficients of low-molecular-weight substances is greater the larger the size of the diffusant molecule. *D* decreases exponentially with increase of *V**, where *V** is the product of the cross-section of the diffusant molecule and the length of the jump in the activated diffusion model[20]. Naturally, for the diffusion of oxygen, the dependence of the diffusion coefficient on the load is significantly less (for example, the orientational stretching of PP to $\lambda = 7$ decreases the translational diffusion coefficient of a very large nitroxy-radical, namely the 2,2,6,6-tetramethylpiperidinoxy-radical, by a factor of approximately 100 at room temperature[29]), while the diffusion coefficient of nitrogen falls only severalfold under these conditions[28].

Thus one can assume that the influence of the external load on the diffusion coefficient of oxygen in oriented specimens [and hence also on the rate of reaction (1)] is small. It may be expected that, under the conditions of plastic deformation, the rate of reaction (1) increases. (It is known, for example, that, in the absence of a mechanical influence at 77 K, alkyl radicals are not converted into peroxy-radicals in an oxygen atmosphere; on the other hand, when various polymers are vibromilled at 77 K in an atmosphere of oxygen, peroxy-radicals are formed, which is evidently associated with the enforced acceleration of the diffusion of oxygen in the specimen[78].)

At fairly high oxygen pressures the rate of reaction (1) influences the kinetics of the oxidation of polyolefins only indirectly (see below) because the rate-limiting stage in the propagation of kinetic chains is reaction (2).

In polyolefins reaction (2) can proceed intramolecularly and intermolecularly. In PE and its low-molecular-weight analogues the main pathway in reaction (2) is apparently intermolecular. Indeed, according to Ivanchenko et al.,[79] the rate constant for the abstraction of a hydrogen atom from the PE macromolecule in solution (in the presence of the cumenylperoxy-radical as the acceptor) at 115 °C amounts to 0.12 litre mol^{-1} s^{-1}, which corresponds to a lifetime of the peroxy-radical in PE, relative to the intermolecular chain transfer reaction, of ~ 2.5×10^{-2} s. (Account is taken of the fact that the reactivity of the secondary peroxy-radical in PE is ~ 3 times higher the reactivity of the tertiary cumenylperoxy-radical, and the concentration of the reactive C–H bonds in block PE is 142 mol kg^{-1}.[80] This estimate for the "ideal" intermolecular reaction (2) was made without taking into account the specific features of the reactions in the solid phase where the constant may be significantly lower.)

The lifetime of the peroxy-radical of PE, in relation to the intramolecular radical substitution reaction, can be estimated from data obtained in a study[81] whose authors investigated the transition $RO_2^{\cdot} \rightarrow R^{\cdot}$ in PE–urea complexes, where it proceeds strictly intramolecularly. Extrapolation of the above data[81] to 115 °C yields the lifetime of the peroxy-radical PE in relation to the "ideal" intramolecular reaction (2), which amounts to ~ 3×10^2 s, i.e. higher by almost four orders of magnitude than the lifetime in relation to the intermolecular reaction. Such differences are apparently caused by the low probability of the activated complex with the optimum linear structure in the section of the chain having the *trans*-zig-zag conformation in PE–urea complexes. Examination of the possibility of reaction (2) in the *trans*-zig-zag PE model shows that the formation of a linear activated complex requires the distortion of the *trans*-zig-zag as a consequence of a change in the angles of internal rotation or the distortion of the valence angles. This factor probably determines the high activation energy for the intramolecular reaction (2) in the PE–urea complex (24.6 kcal mol^{-1}[81]), while in n-decane the activation energy for the abstraction of a hydrogen atom by the cumenylperoxy-radical is 17.5 kcal mol^{-1}.[80]

The preferentially intermolecular course of reaction (2) in PE is also indicated by the large fraction of the monomeric (not linked by hydrogen bonds) hydroperoxide formed on oxidation: whereas mainly bound hydroperoxide is formed in substituted poly-α-olefins (PP, poly-4-methylpent-1-ene-P-4-MP-1) on oxidation, in PE the concentration of the free hydroperoxide exceeds that of the bound form[82].

A necessary condition for the intermolecular transfer of kinetic chains is molecular mobility which ensures the encounter of the peroxy-macroradical with a neighbouring macromolecule. As shown in Sections II.3 and II.4, orientational stretching decreases the segmental mobility of the macromolecules in the amorphous phase, which can influence the rate of reaction (2). Indeed, according to the data of Rapoport et al.,[82] in the radiation-induced oxidation of PE at room temperature the parameter $k_2/k_6^{1/2}$ in oriented PE is lower by a factor of ~ 1.5 than in the isotropic monomer; this is evidently associated with a decrease of k_2, because the destruction of radicals is also controlled by molecular dynamics and for oriented PE the constant k_6 should be lower than for the isotropic polymer (see below).

In contrast to PE, in substituted poly-α-olefins and their low-molecular-weight analogues, reaction (2) proceeds mainly intramolecularly[11,83-85]. Examination of the probability of the intramolecular reaction (2) of a model of the PP macromolecule showed[55] that the reaction is virtually impossible if the radical is localised in the section of the macromolecule having an extended TGT conformation (the same as in PP crystallites): in this case the peroxy-radical is shielded from the neighbouring tertiary C–H bonds of the same macromolecule. Reaction (2) becomes sterically feasible only if the reaction centre undergoes the TGT → TGG evolution.

The formation of the conformation necessary for the reaction can be formally regarded as the "encounter" of a radical in the TGT conformation with a G conformer "diffusing" in the macromolecule. In reality the diffusion process constitutes a concerted transition of the type $\mathrm{TGTGTGT} \underset{k_{-r}}{\overset{k_r}{\rightleftharpoons}} \mathrm{TGGTGGT}$. The cooperative nature of the transition is due to the fact that the TT and GGG conformations in PP are forbidden (the former as a consequence of the "overlap" of the methyl groups and the latter due to the effect of the excluded volume). Attention should be drawn to the fact that the number of G conformers on the right-side of the scheme presented exceeds their number on the left-hand side, i.e. conformational transitions of this kind require the presence of "superfluous" G conformers in the macromolecule (compared with their number in the fully extended helical TGT sequence). The number of *gauche*-conformers in a given section of the macromolecule is determined by the ratio of its contour length to the distance between its ends and for each macromolecule in the amorphous phase of an amorphous-crystalline polymer is specified "genetically" at the instant of crystallisation or orientational extension.

Formally, reaction (2) can be considered from the standpoint proposed[86,87] for the kinetic description of bimolecular solid-phase reactions. Reaction (2) is described as a result of the reaction in the radical–GG conformer pair:

$$\mathrm{GG} + \mathrm{R\dot{O}_2} \underset{k_{-r}}{\overset{k_r}{\rightleftharpoons}} [\mathrm{R\dot{O}_2}(\mathrm{GG})] \xrightarrow{k_x} \mathrm{ROOH}\ .$$

Assuming that $k_r \cong k_{-r}$, we obtain the following expression for the rate of reaction (2) in the quasi-stationary approximation:

$$w_2 = \frac{k_x k_r}{k_x + k_r} [\mathrm{GG}] [\mathrm{R\dot{O}_2}] \equiv k_{\mathrm{eff}} [\mathrm{GG}] [\mathrm{R\dot{O}_2}]\ .$$

If the rate-limiting stage is the "encounter" of the GG conformer with the radical, then $k_{\mathrm{eff}} \cong k_r$; if the reaction in the pair is rate-limiting (i.e. not every collision of the radical with the GG conformer results in reaction), then $k_{\mathrm{eff}} \cong k_x$; in the intermediate case k_r and k_x are added together in accordance with the law of kinetic resistances.

In any case the rate of the intramolecular reaction (2) is proportional to the concentration of the GG conformers in the macromolecule. In the amorphous phase of amorphous-crystalline polymers there is always a distribution of sections of the macromolecules with respect to the contour length and hence a distribution with respect to the concentrations of the GG conformers§. In the oxidation of amorphous-crystalline polymers one should therefore observe a distribution with respect to the constants k_2 and the latter, determined on the basis of the overall kinetics of the oxidation reaction[89,90] (and incidentally also the constants k_1 and k_6) are effective average quantities for the given distribution.

The lowest constant k_2 is to be expected in the crystalline phase of PP where the unreactive TGT conformation predominates and constitutes "the elementary unit" of the helix and the characteristic reaction time is probably the expectation time for the formation of a defect in the helix at the site of the location of the radical. Reaction (2) in the crystalline phase of PP has been investigated[91] in the temperature range 270–300 K; an estimate of the effective value of k_2^{cr} from the results of this investigation yields ~ 2×10^{-5} s^{-1}, which is lower approximately by three orders of magnitude than k_{eff} for the amorphous phase of PP[89,90]. Such differences between the rates of reaction (2) in the crystalline and amorphous phases of PP are apparently a result of the "conformational inhibition" of the reaction in the crystalline phase[61]. The existence of a distribution with respect to the constants k_2 in PP is indicated by the results of a study[92] in which the kinetics of the destruction *in vacuo* of the peroxy-radicals of PP, obtained by γ-radiolysis at −78 °C and at room temperature, were investigated. The authors[91] fitted sets of three (irradiation at −78 °C) or two (irradiation at room temperature) exponential functions to the kinetic curves obtained. The plots of c/c_0 against lg τ, based on the results of the above study[92], are straight lines which may be evidence in support of the existence of a distribution function for the reactive species with respect to the constants k_2; the lowest constant k_2 agrees in order of magnitude with the value determined[91] for the crystalline phase of PP.

In the orientation stretching of polymers and following the application of an additional load to them, the conformers are redistributed (there is a decrease of the fraction of GG pairs and an increase of the fraction of TG pairs) and the overall concentration of the coiled conformers decreases (see below). As was to be expected, this results in a decrease of the average effective value of the constant k_2[89] by (a factor of 3–4 in oriented PP compared with the isotropic polymer). Although the absolute changes in the effective constant k_2 in oriented PP are small, the shift of the distribution towards lower values of the constants for the extended chains,

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§ Attempts to establish the character of the distribution of sections of macromolecules with respect to length have been made[88]. Histograms of the concentrations of the free radicals formed in the stepwise deformation of PA-6 fibres were constructed. Unfortunately the results obtained are not unambiguous because it is still not clear whether there is a direct correlation between the concentration of the free radicals detected and the concentration of the ruptured macromolecules.

enriched in the unreactive TGT conformers, plays a decisive role in the strength of the material and its change during oxidative degradation, which are very important characteristics.

(c) Reaction (2) and the variation of the strength characteristics of PP in the oxidation process. The strength properties of amorphous-crystalline polymers are determined by the "tail" of the distribution of sections of the macromolecules in the amorphous phase with respect to lengths, which corresponds to the shortest and therefore the most extended chains incorporating the smallest number of coiled *gauche*-conformers. According to Kaush and De Vries[88], the fraction of fully extended macromolecules in PA-6 fibres, responsible for the modulus of elasticity and the strength properties of the specimen, is 1.1%, while 98.6% is the fraction of chains in the unextended state (see the preceding footnote concerning these results). The greater the degree of extension, the higher the fraction of the short-chain "tail" of the distribution, the greater the number of the fully extended macromolecules, and the higher the initial strength of PP[58]. It follows from the above that the probability of the intramolecular reaction (2) involving such macromolecules should be a minimum; reaction (2) in polyolefins results in the formation of hydroperoxy-groups whose thermal decomposition is usually accompanied by the degradation of the macromolecules and serves as the main source of the decrease of the molecular weight in autoxidation[93,94]. If reaction (2) proceeds intramolecularly, a hydroperoxide block is formed. According to Shlyapnikova and Shlyapnikov[94], the probability of the degradation of the macromolecule on decomposition of the hydroperoxide increases with increase of the length of the block:

$$\rho_d = 1-(1-\rho_1)^{\nu_{bl}},$$

where ρ_1 is the probability of the decomposition of a single hydroperoxy-group without the degradation of the macromolecule and ν_{bl} is the length of the block.

The presence of extended conformers prevents the intramolecular propagation of the kinetic oxidation chain; the more extended the chain, the smaller the number of GG conformers in it, and the lower the probability of the intramolecular reaction (2). Short hydroperoxide blocks or isolated hydroperoxy-groups would therefore be expected to form on the extended macromolecules [as a result of the intramolecular reaction (2), whose rate constant has been shown, in relation to low-molecular-weight analogues of PP, to be significantly lower even in the liquid phase than the intramolecular constant k_2 (Mill and Montorsi[11]]; the intermolecular reaction should be even slower in the solid polymer, where its rate is limited by the rate of encounters of the reactants, one of which is the stressed polymer chain, and, apart from diffusion-dependent obstacles, there is also steric hindrance to the reaction[13].

The isolated hydroperoxy-groups are decomposed several times more slowly than the block groups[84]. Consequently both the formation and the decomposition of the hydroperoxy-groups are retarded on extended macromolecules, which should lead to a sharp fall of the rate of the oxidative degradation of the extended macromolecules compared with the degradation of the coiled macromolecules. Since extended macromolecules are in fact responsible for the strength properties of the polymer, for the same degree of oxidation one should expect a smaller diminution of the strength of the specimens having a higher concentration of extended macromolecules, i.e. specimens which are more highly oriented. It has been shown[55] that this is indeed the case (Fig.10).

Formally, the amorphous phase of oriented PP can be divided into two unequal parts: in the larger part enriched in the coiled conformations (the "soft" part), there is rapid intramolecular propagation of the kinetic chains leading to the formation of hydroperoxide blocks, and degradative processes develop (this part of the polymer is responsible for the overall kinetics of the absorption of oxygen), while in the smaller ("hard") part, enriched in the extended conformations, the intramolecular propagation of kinetic chains is inhibited and their oxidative degradation is much slower; the absorption of oxygen by these macromolecules does not contribute appreciably to the overall oxidation kinetics but they are in fact responsible for the retention of the strength properties of the specimens undergoing oxidation. The retention of non-degraded extended macromolecules even for high degrees of oxidation of oriented PP has been confirmed in experiments involving the measurement of the repeated durability of unannealed and annealed PP specimens[61] (see below).

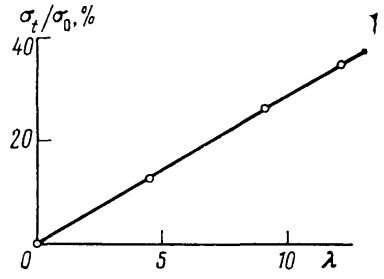


Figure 10. Dependence of the relative strength of PP on the degree of extension for absorption of O_2 at a concentration of 0.5 mol kg^{-1}.[55]

Thus a mechanical stress, leading to a decrease of the diffusional mobility of the polymer matrix and altering the set of conformations of the macromolecules in favour of the extended isomers, causes a decrease of the effective rates of both propagation reactions of the kinetic oxidation chains [reactions (1) and (2)].

(d) The branching of kinetic chains. The degenerate branching of kinetic chains in polyolefins takes place as a result of the thermal decomposition of the hydroperoxy-groups into radicals. Since side groups are decomposed in this reaction, a mechanical stress should not influence significantly the decomposition rate constant. Nevertheless, the rate of degenerate branching of kinetic chains in oriented PP proved to be significantly lower than in the isotropic polymer[57,95]. This is associated with the decrease of the yield of the branching agent—the hydroperoxide (calculated per mole of the absorbed oxygen).

Fig.11 presents the kinetic curves for the accumulation of hydroperoxide in the autoxidation of PP specimens with different degrees of orientational extension. Evidently a decreasing concentration of the accumulated hydroperoxide corresponds to the same amount of absorbed oxygen in the specimens with an increasing degree of extension. It has been shown[57] that this is not associated with the increase of the rate of the thermal decomposition of the hydroperoxide in the oriented specimens. The observed effect is caused by the induced decomposition of the hydroperoxy-group

under the influence of the alkyl macroradical present in it in the β-position—the isomerisation of the β-hydroperoxyalkyl radical [see the scheme below illustrating the sequence of reactions (2)]. The addition of oxygen to the alkyl macroradical, resulting in the formation of a "stable" hydroperoxy-group, competes with the isomerisation reaction. Within the framework of this mechanism, the yield of the hydroperoxide per mole of absorbed oxygen (α) is defined by the expression

$$\alpha = k_1[O_2]/(k_1[O_2] + k_5) ,$$

i.e. depends on the rate of reaction (1). Thus the rate of reaction (1) diminishes as a result of the orientational stretching of PP: the induced decomposition of the hydroperoxide begins to complete successfully with the addition of oxygen to the alkyl macroradical, which leads to a decrease of the parameter α. In this case the kinetic chain propagation reaction [reaction (2)] results in the preferential formation of an alcoholic hydroxy-group and an alkoxy-macroradical and not the branching agent (hydroperoxide) and an alkyl macroradical. The validity of the proposed interpretation is confirmed by the dependence of α on the oxygen pressure in the oxidation reaction[96-98].

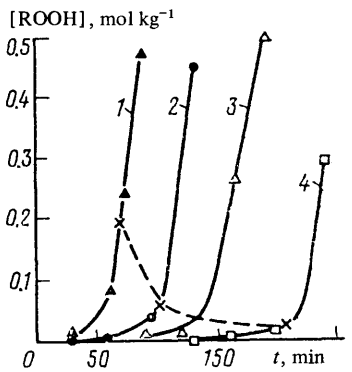


Figure 11. Kinetic curves for the accumulation of hydroperoxide in the autoxidation of PP with different degrees of extension (130 °C, p_{O_2} = 600 mmHg)[27]; the points corresponding to the absorption of oxygen at a concentration of 0.5 mol kg^{-1} are joined by a dashed line; λ: 1) 0; 2) 4.5; 3) 7; 4) 9.

The decrease of the yield of the hydroperoxide per mole of the absorbed oxygen in oriented PP specimens should lead to an increase of the induction period of the autoxidation relation, which has been observed experimentally[58] (see below).

(e) Termination of kinetic chains. In solid polymers the rate of destruction of macroradicals is limited by the rate of their encounters and is sensitive to the intensity of molecular movements[8]. In order to account for the experimentally observed high rates of destruction of macroradicals in solid polymers, the dependence of the rates of destruction on molecular mobility of the system, the anomalously high activation energies for the degradation process, and the compensation effect, several models have been proposed and have been examined critically[8].

In the amorphous phase of the isotropic PP the rate of destruction of peroxy-radicals ($k_6 \cong 10$ litre mol^{-1} s^{-1})[88,99] exceeds by 2–3 orders of magnitude that observed in the crystalline phase of PP even at room temperature[100] (the constant k_6 is undoubtedly an effective quantity; the activation energy is E_6^{PP} = 28.5 kcal mol^{-1}). Orientational stretching, which leads to a decrease of the average segmental mobility in the amorphous phase of the polymer, induces a decrease of the rate of destruction of the radicals[89, 101,102]. The data for PP[89] are presented in Fig.12. They correspond to the destruction of radicals in elastically deformed and entropically stressed PP. An entirely different dependence of the rate of destruction of radicals on the stress is to be expected in the case where the polymer undergoes plastic deformations: the enforced mixing of macromolecules under the influence of mechanical stresses increases the rate of their encounters and the rate of their destruction[103-105]. The destruction of radicals in the crystalline phase of PE and PP fibres at the instant of deformation of the crystallites¶ has been observed[104] (Fig.13).

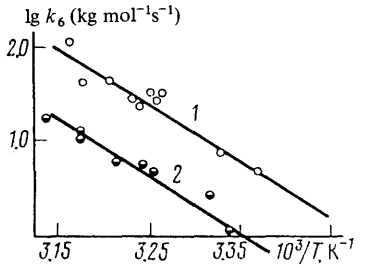


Figure 12. Temperature variation of the rate constant for the destruction of peroxy-radicals in PP: 1) isotropic; 2) oriented (λ = 8)[88].

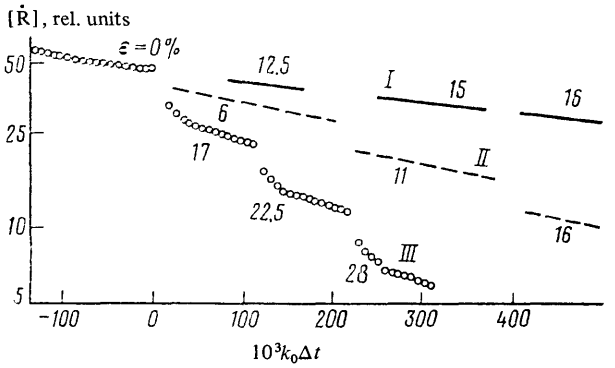


Figure 13. The influence of the degree of deformation of polymers ε on the destruction of radicals in irradiated and heat-treated PA-6 (I), PP (II), and PE (III) fibres; the reduced time is plotted along the abscissa axis; k_0 = rate constant for the destruction of radicals with zero deformation; Δt = time from the onset of deformation[14] (p.240).

¶ This is most probably associated with the formation and migration of defects in the crystal structure at the instant of deformation of the specimen.

An analogous effect has been investigated by Radtsig and Rainov[105], who showed that the reaction involving the destruction of the peroxy-radicals of polystyrene (PS) (which proceeds with a kinetic arrest at a temperature below T_g) can be restarted if the polymer is subjected to a brief plastic deformation at 77 K: the migrations of the macroradicals and macromolecules alter the local environment of the macroradicals and restore the initial distribution of the radicals with respect to reactivity. Thus the plastic deformation of the polymer should promote an increase of the rate of destruction of the macroradical. In PP this effect can be enhanced also by the fact that, as will be shown below, in the region of plastic deformations the initiation of kinetic chains proceeds preferentially via reaction (0) with formation of terminal macroradicals, which are more mobile and reactive than the internal macroradicals.

The results of the study of the influence of the stretching stresses on individual stages of the chain oxidation show that in the region of both elastic and plastic deformations the stresses accelerate the initiation reactions (0) and (0') and inhibit the kinetic chain propagation reaction (2), while reaction (1) and the kinetic chain termination reaction (6) are inhibited in the region of elastic deformations and are accelerated in the region of plastic deformations; the reaction involving the degenerate branching of the kinetic chains [reaction (3)] is inhibited in the region of elastic deformations.

The influence of stretching stresses on the rate of the overall oxidation depends on the role which each of the above stages plays in the overall chain process.

2. The Influence of Stretching Mechanical Stresses on the Overall Rate of Oxidation of Polyolefins

We shall consider initially the effects of orientational extension in the kinetics of the oxidation of polyolefins and then the effects of an external load applied to the oriented specimens and hence the problem of the durability and mechanism of the decomposition of polyolefins subjected to the joint action of mechanical stresses and an oxidising medium.

(a) The effects of orientational extension in the overall kinetics of the oxidation of polyolefins. This process has been studied in detail in a series of investigations[27,55–58,60,82,89,95,98,106] and has been examined critically in a review[26]. Here we shall deal briefly with the main results. Fig.14 presents the kinetic curves, for the absorption of oxygen in the autoxidation of unannealed and annealed PP films with different degrees of extension, and their linear forms. The kinetic parameters of the oxidation process are compared in Table 3 with the structural-mechanical parameters of the oriented specimens. The kinetics of the oxidation of the oriented PP are characterised by the following main features:

(1) the induction period in the oxidation of unannealed PP specimens increases exponentially with increasing degree of extension (Fig.14a) (an analogous relation has been observed for polyamide fibres[107]); (2) the differences between the initial rates of oxidation (reflected in the increase of the induction period with the degree of orientation) persist along the autocatalytic sections of the kinetic curves: the slopes of the linear forms of the curves diminish with increasing degree of extension (Fig.14c); (3) the maximum rates of oxidation are independent of the degree of extension; (4) starting with a specific duration of oxidation, the kinetic curves for the absorption of oxygen can be satisfactorily fitted by parabolas and the linear forms of the kinetic curves do not pass through the origin of coordinates [it has been suggested that the time interval t_0 obtained by extrapolating the linear forms of the curves (Fig.14c) to the abscissa axis be referred to as the true induction period of the uninhibited oxidation of PP[106]]; during the period t_0, the oxidation of the polymer develops at a very low rate; (5) annealing leads to the smoothing out of the differences between the oriented and isotropic specimens.

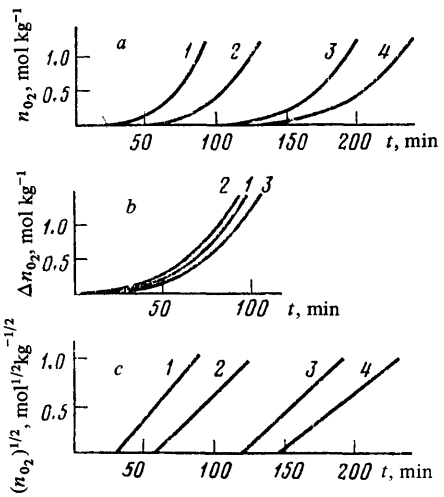


Figure 14. Kinetic curves for the absorption of oxygen in the autoxidation of PP: *a*) unannealed specimens; *b*) annealed specimens; *c*) linear plots corresponding to the kinetic curves; λ: 1) 0; 2) 4.5; 3) 9; 4) 12 (130 °C, p_{O_2} = 600 mmHg)[58].

The following main conclusions have been reached on the basis of the data presented.

1. The decrease of the initial rate of oxidation (the increase of the induction period) as a result of the orientational extension is not associated with a change in the degree of crystallinity, as is usually assumed (see, for example, Winslow et al.[108]): during annealing, the degree of crystallinity increases appreciably (from 64 to 76%), while the induction period of the oxidation reaction actually diminishes.

2. The changes in the oxidation kinetics are due to the presence of stressed extended macromolecules in the amorphous phase: annealing, leading to the relaxation of the internal stresses and the restoration of the compact conformations of the macromolecule[58,108], eliminates the differences between the oriented and isotropic specimens. Chemical relaxation of internal stresses, associated with the rupture of the extended macromolecules during the oxidation process itself, leads to the same result (this explains the equality of the maximum rates of oxidation for specimens with different degrees of extension).

Thus the main effect of orientational extension in the kinetics of the oxidation of PP is a significant increase of the induction period of the autoxidation reaction. An analogous phenomenon has been observed in the oxidation of oriented poly-4-methylpent-1-ene (P-4-MP-1)[110]. Differences between the kinetics of the absorption of oxygen by isotropic and oriented specimens were not observed in the autoxidation of PE at 130 °C,[82] which is natural because at this temperature relaxation processes take place vigorously in PE.

The data presented in the previous Section concerning the changes in the kinetic parameters of the individual stages of the chain oxidation of stressed PP show that, when PP is oriented, the effective rate constants for the propagation and termination of kinetic chains (k_2 and k_6) decrease in such a way that the parameter $k_2/k_6^{1/2}$, which determines the rate of the oxidation reaction at an advanced stage, diminishes slightly (by a factor of ~ 1.5 in the specimen with $\lambda = 4.5$, obtained by stretching an isotropic specimen subjected to preliminary oxidation). The changes in the initial rate of reaction exceed significantly the changes in the parameters $k_2/k_6^{1/2}$ (for example, the induction period of the oxidation reaction involving the specimen with $\lambda = 12$ increases by a factor greater than 4 compared with the isotropic specimen—see Table 3).

Table 3. Relation between the structural-mechanical parameters of oriented PP specimens and the kinetic parameters of their autoxidation (130 °C, p_{O_2} = 600 mmHg).[58]

λ	$10^3_s{}^0 r_{corr}$,	α_{cr}, %	σ, MPa	E, MPa	τ_{ind}, min	$10^6 b$, $mol^{1/2} kg^{-1/2} s^{-1}$	$10^4 w_{max}$, $mol\ kg^{-1} s^{-1}$
0	5.4/5.4	58/70	0	2	40/30	2.8/2.1	6.9/4.9
4.5	5.7/5.4	66/74	13	40	75/30	2.4/—	6.2/4.5
9.0	7.9/5.4	64/76	86	290	140/35	2.1/—	6.2/4.5
12.0	9.3/5.4	65/71	215	660	170/40	1.9/—	6.2/5.0

Note. The values for the unannealed and annealed specimens are given in the numerator and denominator respectively. Notation: τ_{corr} is the correlation time of the rotational movement of the probe radicals (the 2,2,6,6-tetramethylpiperidin-1-oxy-radical) at 60 °C, α_{cr} the degree of crystallinity, σ the stress in the orientational extension, $E = (2\lambda + 1)(d\sigma/d\lambda)$ the conventional rigidity, τ_{ind} the induction period of the autoxidation reaction, b the slope of the linear form of the kinetic curve for the absorption of oxygen in Fig. 14c, and w_{max} the maximum rate of absorption of oxygen.

The causes of the change in the induction period of the oxidation reaction during the orientational extension of PP have been examined[95,106]. However, before proceeding to their discussion, one must deal briefly with the question why an induction period arises at all in the uninhibited oxidation of PP and P-4-MP-1 or, in other words, why the kinetics of the initial stage of the oxidation reaction differ from the characteristics of the reaction at an advanced stage.

The derivation of kinetic information about the process occurring during the induction period presents considerable experimental difficulties, because the rates and degrees of oxidation are then very low. The absence of the necessary kinetic information does not at present permit unambiguous answers to the question posed. It has been shown[106] that the kinetic features characteristic of reactions with degenerate branching and quadratic termination of the kinetic chains are established only after the accumulation in the specimens of specific concentrations of the hydroperoxide (2×10^{-2} mol per kg of the amorphous phase, 80 °C, 760 mmHg O_2), which are approximately equal for the isotropic and oriented specimens (Fig. 15). It has been suggested[106] that at lower concentrations the hydroperoxide in PP has a low initiating capacity and is not the main source of radicals; the initiation reaction proceeds via the direct interaction between oxygen and the macromolecules [reaction (0)].

The results obtained recently in the study of the kinetics of the autoxidation of PP at elevated oxygen pressures[111] may serve as confirmation of the ideas described: it was found that the induction period decreases with increasing oxygen pressure over the entire range of pressures (from 0.02 to 4.24 MPa), while the maximum rate of accumulation of carbonyl groups virtually ceases to depend on the oxygen pressure already at $p_{O_2} \cong 0.45$ MPa. The activation energy for the induction period in the range 60–90 °C proved to be 24 kcal mol^{-1}. The low initiating capacity of the hydroperoxide formed in the initial stage of the oxidation reaction may be associated with the fact that its decomposition proceeds either as the unimolecular reaction

$$ROOH \xrightarrow{k_{s1}} R\dot{O} + \dot{O}H$$

(activation energy 35 kcal mol^{-1}, low values of k_3) or via the reaction

$$ROOH + RH \xrightarrow{k_{s2}} [R\dot{O} + \dot{R}] + H_2O \rightarrow \delta\dot{R}\ ,$$

in which rapidly recombining alkyl and alkoxy-macroradicals are formed (low degree of liberation of radicals from the cage, low values of δ). At higher concentrations the hydroperoxide apparently decomposes in intermolecular pairs linked by a hydrogen bond:

$$ROOH + ROOH \xrightarrow{k_{s3}} [R\dot{O}_2 + R\dot{O}] + H_2O \rightarrow \delta'\dot{R}\ .$$

The maximum rate of initiation corresponds to this reaction[86]. The increase of the initiation rate constant approximately by an order of magnitude with increase of the hydroperoxide concentration is observed also in the liquid phase: in the initial stage of the oxidation of n-decane and in the decomposition of t-butyl hydroperoxide[112].

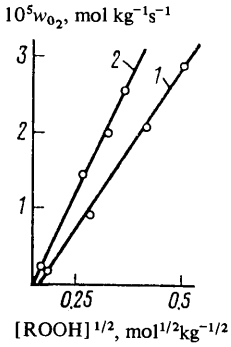


Figure 15. Dependence of the rate of absorption of oxygen on the concentration of the hydroperoxide for isotropic (line *1*) and oriented ($\lambda = 9$) (line *2*) PP films (80 °C, p_{O_2} = 760 mmHg)[107].

An alternative hypothesis concerning the causes of the induction period in the uninhibited oxidation of PP has been put forward[113]. It has been shown[114,115] by the EPR method that the rate of destruction of peroxy-radicals decreases with increase of the hydroperoxide concentration in PP subjected to preliminary oxidation: at room temperature k_6 falls from 170 to 5.2 kg mol^{-1} s^{-1} with increase of the hydroperoxide concentrations from 2.5×10^{-3} to 1×10^{-1} mol kg^{-1}, but, after the accumulation of hydroperoxide to give a concentration of 4×10^{-2} mol kg^{-1}, the constant k_6 changes only slightly. If it is assumed that the constant k_2 remains

unchanged during oxidation, then the changes in k_6 lead to an increase of the parameter $k_2/k_6^{1/2}$ with the degree of oxidation.

In principle, this can explain the difference between the kinetics of the initial stage and the advanced reaction. However, the induction period in the oxidation of PP is observed also at high temperatures (130 °C and above) where the constants k_6 are close to the "chemical" rate constant for the destruction of tertiary radicals in the liquid phase even for the oxidised polymer and it is difficult to expect higher values of k_6 in the initial stage. We therefore believe that the hypothesis of a low initiating capacity of the hydroperoxide formed in the initial oxidation stage is more likely. In one way or another, the establishment of the kinetic features characteristic of the advanced reaction is associated with the accumulation in the specimens of a hydroperoxide up to a specific concentration, which is virtually the same for isotropic and oriented specimens (Fig.15).

It was shown in Section III.1 that the rate of formation of the hydroperoxide falls when PP is oriented as a consequence of the decrease of the yield of the hydroperoxide per mole of absorbed oxygen. This factor is apparently the main cause of the increase of the induction period in the oxidation of PP subjected to orientational extension[95,106]. The decrease of the yield of the hydroperoxide is a consequence, in its turn, of the structural-physical changes occurring during the orientational stretching and is associated with the decrease of the rate of microdiffusion of oxygen in the polymer. This results in an increase of the rate of the induced decomposition of the hydroperoxide, which takes place without branching of the kinetic chains. We emphasise yet again that the oxidation of the entropically stressed specimens is slower than that of the unstressed specimens. The relaxation of stresses and the restoration of the compact conformations of the macromolecules in the amorphous phase of the oriented specimens smooth out the structural-physical differences between the isotropic and oriented specimens and increase the rate of oxidation of the latter (Table 3). This has important and interesting consequences for the kinetics of the oxidation and the durability of the specimens subjected to an external stretching load.

(b) The kinetics of the oxidation, durability, and mechanism of the decomposition of polyolefins subjected to an external stretching load. The mechanical load alters the structure of the molecular-dynamic properties of polymer matrices (see Section II); it is therefore natural to expect that the kinetics of the oxidation of polymers subjected to an external load will differ from the kinetics of the oxidation of specimens without an applied load. A series of studies devoted to this question have been carried out on oriented PP[59,72,73,116,117]. The specimens were maintained under different loads until rupture under the conditions of vigorous thermo-oxidative degradation and the durability of the polymer was compared with the concentrations and proportions of the oxidation products in the ruptured specimens. It was shown that, in the oxidation of PP subjected to an external stretching load, there exists a range of stresses in which the durability of the polymer depends only slightly on the load[59] and can actually increase as the latter is increased[117], but under these conditions the durability *in vacuo* is smaller by many orders of magnitude, i.e. is determined wholly by the rate of the thermo-oxidative degradation processes[71-73]. As an illustration, Fig.16 presents (on the basis of the data of Livanova et al.[73]), the durability isotherms (*a*) and curves relating to the rate of the steady creep to the stress (*b*) in oxygen and *in vacuo* for different PP specimens. The durability isotherms can be arbitrarily divided into three sections: along section I, the durability is determined by the rate of the thermo-oxidative chain degradation, along section II, by the sum of the rates of the mechanoinitiated and oxidative degradation, and along section III, solely by the rate of the mechanodegradation of the macromolecules carrying the load (which diminishes in a certain range with increase of the stress as a consequence of processes involving the orientational strengthening of the polymer). Accordingly, the durability increases significantly along section I after the introduction of inhibitors[60,71], while along section III it remains unchanged (Fig.7).

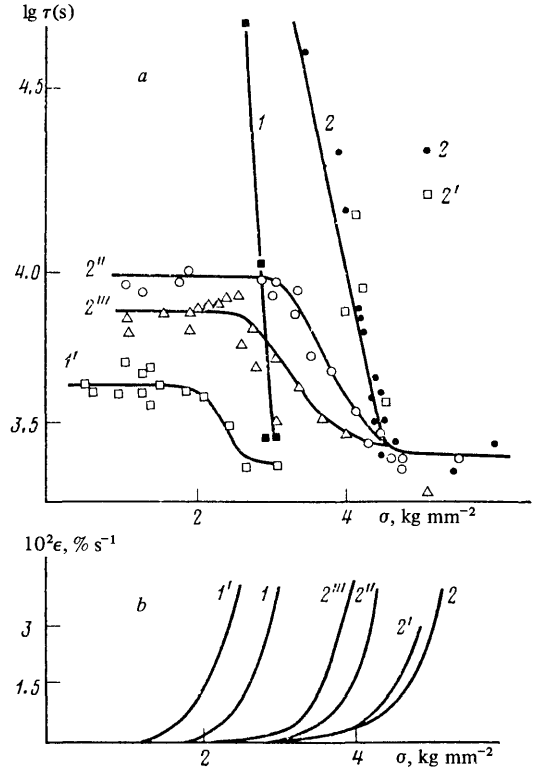


Figure 16. Durability isotherms (*a*) and the dependence of the rate of steady creep on the stress (*b*) at 130 °C for $\lambda = 5$ (curves *1* and *1′*) and 7 (curves *2* and *2′*–*2‴*) in oxygen (curves *1′*, *2″*, and *2‴*) and *in vacuo* (curves *1*, *2*, and *2′*) for unannealed (curves *1*, *1′*, *2*, and *2′*) and annealed (curves *2′* and *2‴*) specimens[73].

Fundamentally new results have been obtained[60,116] in a study of the concentration and distribution of the oxidation products in PP specimens oxidised under an external load. More than 100 specimens differing in the degree of extension, the initial structure (unannealed and annealed), and in the external stress (σ = 5–70 MPa) were investigated. In these studies the distribution of the oxidation products in the film was determined by scanning the specimen with a beam of infrared light focussed on to an area of 1 mm^2. We shall now describe the main results.

1. With increase of the applied stress, the transition from elastic deformations to creep deformations entails a change in the concentration and composition of the oxidation products

in the zone of the rupture of the specimens, indicating a change in the initiation mechanism: initiation via reaction (0) is gradually replaced by initiation via reaction (0'). This is accompanied by a decrease of the length of the kinetic oxidation chains and, under the conditions of fairly high stresses, the oxidation reaction passes from the chain to the non-chain regime. Fig.17 presents (on the basis of the data of Rapoport and co-workers[60,116]) the infrared spectra of the ruptured specimens in the region of the vibrations of the carbonyl and hydroxy-groups. For stresses corresponding to elastic deformations, the shape of the absorption band of the carbonyl groups in the stressed PP hardly differs from that of the band in the spectrum of the polymer oxidised without an external load; the band maximum at 1710 cm^{-1} corresponds to the C=O stretching vibrations in ketones (Fig.17*a*, spectrum *1*). With increase of the stress, the maximum shift towards higher frequencies, whereas for stresses corresponding to plastic deformations the maximum is observed at 1740 cm^{-1}, which indicates the predominant formation of aldehyde groups (Fig.17*a*, spectrum *3*).

The changes in the spectrum of the carbonyl groups occurring as the deformation regime is altered are accompanied by a sharp diminution of the concentration of hydroxy- and hydroperoxy-groups. In specimens oxidised under the conditions of plastic flow, where the aldehyde groups are virtually the only carbonyl oxidation products, the hydroperoxide cannot be determined iodometrically and the ratio of the concentrations of the aldehyde and hydroxy-groups is ~ 1:1, which corresponds to the ratio which should be obtained in the disproportionation of peroxy-radicals, one of which must be a terminal radical. This implies that in the region of plastic deformations the oxidation reaction virtually passes to a non-chain regime and consists in the formation, oxidation, and destruction of terminal macroradicals.

The data obtained indicate a change in the initiation mechanism: for small stresses, the initiation proceeds via reaction (0) and leads to the formation of middle macroradicals, whose subsequent chain reactions give rise to ketone, aldehyde, hydroperoxy-, and other groups. With increase of the stress, the mechanoinitiated rupture of C–C bonds, leading to the formation of terminal macroradicals, begins to play an increasing role. Evidently this is accompanied by a sharp increase of the rate of termination of the kinetic chains: the terminal radicals are more mobile than the middle radicals formed via reaction (0) and their destruction takes place in the plastically deformed matrix, which, as shown in section III.1, accelerates the process. The non-chain character of the oxidation under the conditions of high stresses is confirmed by the absence of the influence of inhibitors on the durability time in this region of stresses (Fig.7).

2. The fact that the oxidation process under a mechanical stress is local in character, observed by Rapoport and co-workers[60,116], is very important. At the site of the future break in the film, an oxidation centre arises and spreads in the specimen over a distance which depends on the stress in the oxidation reaction and on the structure of the specimen. This results in the establishment of a concentration gradient of oxygen-containing groups in the rupture zone. In the group of spectra *b* and *c* in Fig.17 the lower spectra correspond to the rupture zone of the specimens and the upper spectra to the "matrix" (sites remote from the rupture zone). For a fixed stress, the concentration gradient in the unannealed specimens is always greater than in the annealed specimens (Fig.18, curves *1* and *1a*). For specimens with a fixed structure, the concentration gradient increases sharply with increase of the stress in the oxidation process (Fig.18, curves *1–3*). As a result, the concentration of carbonyl groups, averaged over an area of 1 mm^2 in the rupture zone,

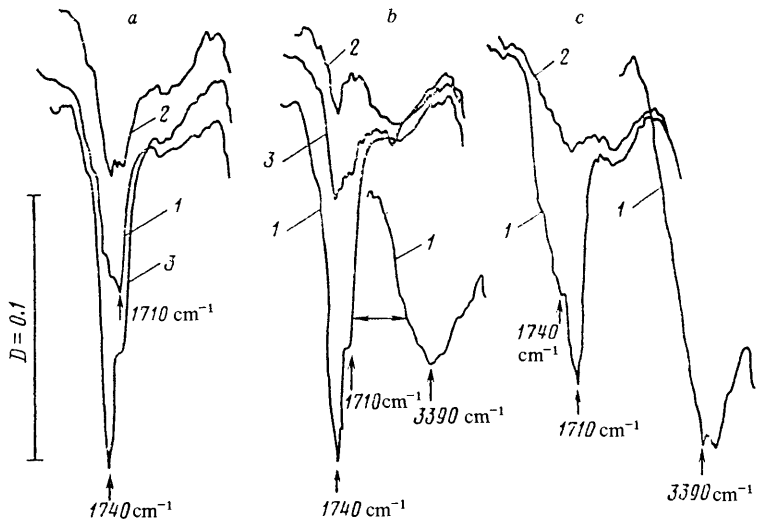


Figure 17. Infrared spectra of PP specimens subjected to an external load up to rupture; *a*) $\lambda = 7$, annealed specimen [σ(MPa): 1) 10; 2) 13; 3) 20]; *b*) the same specimen, $\sigma = 20$ MPa [1) rupture zone; 2) and 3) matrix]; *c*) $\lambda = 4$, unannealed specimen [1) rupture zone; 2) matrix][60,116].

decreases with increasing stress (Fig.19). For example, in unannealed specimens a change of the stress from 10 to 40 MPa (the region of elastic deformations) results in a decrease of the concentration of carbonyl groups in the rupture zone by a factor of 20. The same effect is observed in the annealed specimens. The durability of the specimens in the range of applied stresses 10–40 MPa are very similar. The data presented imply that the average rate of oxidation in the rupture zone diminishes with increasing stress. Since the rate of the initiation reactions increases with increasing stress and the rate of destruction of radicals falls in the region of elastic deformations (Section III.1), the decrease of the overall rate of oxidation with increasing stress can be a result of a decrease of the rate of propagation of kinetic chains induced by the additional enrichment of the amorphous phase of the polymer in macromolecules with extended conformations.

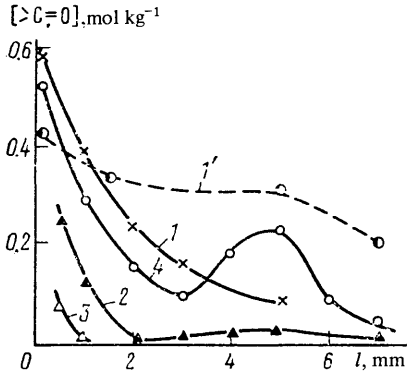


Figure 18. Carbonyl group concentration profile in PP specimens oxidised until rupture: 1)–4) unannealed specimen; 1') annealed specimen; oxidation temperature (°C): 1) and 1') 130; 2)–4) 120; λ: 1)–3) 8.5; 4) 4; σ (MPa): 1) and 1') 10; 2) 20; 3) 29; 4) 5.[60]

In the region of plastic deformations, the concentration of the non-chain oxidation products increases with the stress (Fig.19), which is associated with the increase of the rate of the mechanical initiation of the oxidation reaction. The decrease of the rate of propagation of kinetic chains under load and the increase of the rate of their rupture in the region of plastic deformations actually lead to the transition of the oxidation reaction to the non-chain regime.

3. In the rupture zone of the specimen, not only the concentrations but also the compositions of the carbonyl-containing groups can differ in the "matrix": starting from a specific stress, aldehyde groups predominate in the region remote from the rupture zone, while in the rupture zone ketones as well as aldehydes are often detected (Fig.17*b*). This is apparently associated with the fact that the rupture is preceded by the formation of a large number of microcracks, with relaxation of stress above and below such cracks; the oxidation process develops at these sites in an unstressed polymer, has a chain mechanism, and is accompanied by the formation of ketones. Comparison of spectra *2* and *3* in group *b* (Fig.17) shows that the compositions of the oxidation products differ at individual points in the matrix: in spectra *2* only aldehydes can be detected, while in spectra *3* ketones appear as well. On the basis of the data presented by Rapoport[60], it has been suggested that, at the "point" corresponding to spectrum *3*, a zone corresponding to the release of the load has appeared, which led to the development of chain oxidation and the formation of ketones. The appearance of release of load zones in the stressed polymer is associated with the formation of microcracks. The acceleration of the oxidation on the inner side of the arc-shaped microcracks, formed in the diffusional oxidation of annealed oriented PP specimens, has been observed[118]. Rapoport[60] suggested that the difference between the compositions and concentrations of the oxidation products formed in the stressed zones and in the zones where the load has been released be used as a basis for a method of defectoscopy for stressed PP undergoing oxidation; this possibility has been realised experimentally[116].

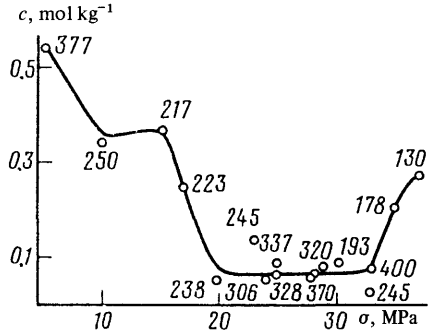


Figure 19. Dependence of the concentration of carbonyl groups in the rupture zone on the stress during oxidation; λ = 7.5; unannealed specimen; oxidation temperature 120 °C; the numbers against the points represent the lifetimes of the specimens in minutes[117].

4. It must be specially emphasised that oxygen-containing groups accumulate at significantly different concentrations at the instant of rupture in the matrices of specimens of different structures undergoing oxidation when subjected to different stresses. For example, the rupture of unannealed specimens frequently occurs when the matrix remote from the rupture zone is still in the induction period of the oxidation reaction (Fig.18, curves *2* and *3*); in the rupture zone profound oxidative degradation takes place under these conditions. On the other hand, at the instant of the rupture of annealed specimens the matrix is highly oxidised (Fig.18, curve *1'*). It is striking that the durabilities of the unannealed and annealed specimens are similar. It is even more striking that their repeated durabilities (the periods before rupture following a second application of the load to parts of the ruptured specimens) are also similar although in the annealed specimens the matrix has been oxidised to a much greater extent from the very beginning of the experiment. Rapoport et al.[116] consider the possible causes of the above effects: (a) the strictly local character of the oxidation of the unannealed stressed specimens; (b) the smoothing out of the structural differences between the annealed and unannealed specimens in the zone of a developing major crack; (c) profound oxidative degradation occurring in the annealed polymer without involving the extended macromolecules carrying the load, which are degraded more slowly and

in accordance with the same kinetic laws as the extended macromolecules in the unannealed polymer. This is an important argument in support of the ideas developed in Section III.1.

5. The significant differences between the concentrations of the oxygen-containing groups accumulating in the matrices of different specimens towards the instant of rupture show how carefully one must approach the development of criteria for macroscopic decomposition: it is very frequently suggested that the accumulation of carbonyl groups up to a specific concentration in the bulk of the specimens be employed as such a criterion for PP[119]; the results of Rapoport et al.[116] show that, as a consequence of the spatial localisation of the oxidation process in stressed PP, the employment of such a criterion would lead to major errors. It follows from the data obtained[116] that, in the study of the kinetics of the rupture of stressed polymers, one should not employ methods yielding values of the measured quantity averaged throughout the specimen.

The spatial localisation of the oxidation process observed in a stressed polymer[60,116] and the dependence of the reaction regime on the size of the stress posed new problems for investigators engaged in predicting the durability of polymer articles under operating conditions (when the polymer is subjected to the joint action of mechanical stresses, oxidising agents, ultraviolet light, etc.). Evidently, in describing the kinetics of such localised processes, one cannot employ the usual mathematical procedures developed for solid-phase reactions (even when account is taken of the distributions with respect to the rate constants). A key question becomes that of the causes and the instant of the spatial localisation of the oxidative degradation. It must be elucidated whether the localisation obtains from the very beginning of the oxidation of the stressed polymer or whether the process proceeds for a time uniformly throughout the bulk of the specimen. We believe that the localisation of the oxidation reaction is an "after-effect" of the opening of the sides of the microcracks and is associated with the acceleration of the oxidation process in the relaxed zones above and below the lips of the microcracks; up to this instant, the degradation can be regarded as proceeding "uniformly" throughout the bulk of the stressed polymer and the formation of a decomposition centre can be treated as a result of the accumulation of random ruptures. In the description of the kinetics of this process, one can therefore use successfully the method described in the literature[120,121].

We shall enumerate briefly the principal results of the studies of Rapoport and co-workers[60,116]: (1) a change in the mechanism of the initiation of the oxidation with increase of mechanical stress has been observed; (2) a change in the reaction regime—a transition from chain to non-chain oxidation—has been noted; (3) the limits of the ability of inhibitors to increase the durability of stressed polymers have been established; (4) the development of the oxidation process from a centre in the stressed polymer, requiring the application of local methods for the experimental study of the kinetics of the decomposition reaction, has been observed; (5) the possibility of the defectoscopy of the polymer undergoing oxidation under the influence of an external load, based on the difference between the concentrations and compositions of the oxidation products formed in the region of the crack and in the "undamaged matrix", has been demonstrated.

Two studies dealing with the kinetics of the oxidation of non-oriented PE[122] and PP[123] specimens subjected to an external load were published in 1982. In the first study[122] PE specimens in the form of "blades", whose widths in the wide and narrow parts differed by a factor of three, which corresponded to stresses differing by a factor of three in relation to the initial section, were oxidised. The ranges of the experimental stresses were 2.9–4 MPa at 70 °C and 1.9–3.1 MPa at 90 °C. The oxidation kinetics were followed from the accumulation of carbonyl groups in the wide and narrow parts of the specimens. For the highest and lowest stresses, no differences were observed between the rates of formation of carbonyl groups in the wide and narrow parts while for intermediate stresses the degree of oxidation of the wide parts of the specimens was always greater; the major crack and the degree of decomposition of the specimens increased in precisely this region, although the true stress was greater in the narrow part. In other words the specimens were not ruptured at the site of the maximum stress but at the sites of the minimum deformation, where the thermo-oxidative degradation developed faster. The results of this study[122] fully confirm the results and conclusions in other investigations[82,60,116]. The lower rate of oxidation of stressed PE in the narrow part is associated with orientation effects and its nature is apparently the same as that of the decrease of the rate of the radiation-induced oxidation of oriented PE[82]. A decrease of the rate of the photochemical oxidation of isotropic PP subjected to an external load has been observed[123].

Thus, under the conditions of orientational extension and an external load, the overall rate of the chain oxidation of polyolefins as a rule diminishes. For stresses which result in a transition of the reaction to a non-chain regime, the overall rate of oxidation increases with increase of the stress as a consequence of the increase of the rate of the mechanical initiation of the radicals.

3. The Influence of Mechanical Stresses on the Kinetics of the Oxidation of Raw and Cured Rubbers by Molecular Oxygen and Ozone

The influence of an external load on the ozone-induced ageing of polyolefins has been studied in the investigations[31,65,66] discussed above in Section III.1. In this Section we shall deal with the specific features of the oxidation of stressed raw and cured rubbers.

The majority of elastomers contain double bonds, which make them more reactive than polyolefins. Elastomers are rapidly oxidised in air and particularly in an ozone–oxygen mixture, which leads to the loss of their operating properties. In recent years this question has attracted increasing attention by investigators in connection with the pollution of the atmosphere and the increase of the content of corrosive components in air. The kinetics of oxidation processes in elastomers are influenced significantly by mechanical stresses[124,125], which was pointed out as early as 1950 by Kuz'minskii[1,2], who called this phenomenon "mechanical activation". The effect of mechanical activation was not related to the breaks in macromolecules, i.e. to mechanical degradation; on repeated deformations (amplitude 75%, frequency 250 cycles min^{-1}), the effect of mechanical activation proved to be much greater than in static deformations (degree of deformation 75%). However, there was no reason to attribute this effect solely to the mechanical activation of oxidation processes, because a dynamic load accelerated equally the rupture of vulcanised elastomers in oxygen and in an inert atmosphere; the effect was more likely to have been associated with the formation and development of microcracks.

Subsequently it was found that mechanical stresses can not only activate but can also inhibit chemical reactions in stressed elastomers[67,126] and the activation effect has been attributed to the decrease of the activation energy for oxidative and thermal processes, while the inhibition effect was attributed to the decrease of the pre-exponential factor.

The existing ideas about the mechanism of the ozone-induced cracking of stressed elastomers have been examined critically in Zuev's book[53]. In this review we are interested in the influence of mechanical stresses on the kinetics of the oxidative degradation of elastomers.

In the ozone-induced ageing of unsaturated vulcanised elastomers, the double bond dissociates. The influence of structural stresses on this process has been investigated on model compounds—cyclo-olefins[64], and a calculation[127] made it possible to explain quantitatively the results obtained by Popov and Zaikov[64]. During the dissociation of the double bond, a steric change takes place in the ~ C(1)–C(2)=C(3)–C(4) ~ unit associated with the rehybridisation of the C(2) and C(3) atoms from the sp^2 state to the sp^3 state; the C(2)–C(3) bond length increases from 1.333 to 1.534 Å, the valence angle decreases from 122.2° to 112.2°, and the angle of internal rotation diminishes from 0° to 60°. Fig.20 illustrates the changes in the distance l between the C(1) and C(4) atoms, not linked by valence bonds, as a function of the reaction coordinate for the *cis*- and *trans*-fragments ~ C(1)–C(2)=C(3)–C(4) ~. For the *trans*-configuration, the C(1)–C(4) distance only increases in the course of the reaction; for the *cis*-isomer, the above distance passes through a minimum. The rate of the ozonisation reaction should therefore be sensitive to the mechanical stress; stretching stresses should accelerate the reaction for the *trans*-configuration of the fragment and should inhibit it for the *cis*-configuration (in the latter case the energy of the transition complex can increase more under the influence of the stretching stress than the energy of the initial state, which should result in an increase of the activation energy for the ozonisation of the *cis*-isomer of raw rubber).

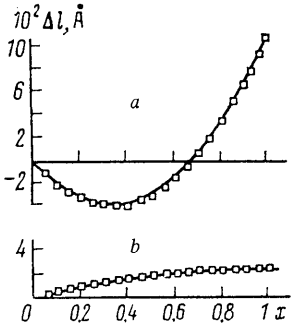


Figure 20. The changes in the C(1)–C(4) distances in the *cis*-forms (*a*) and *trans*-forms (*b*) of the ~ C(1)–C(2)=C(3)–C(4) ~ fragments in the $sp^2 \rightarrow sp^3$ transition of the C(2) and C(3) atoms[68]; x = reaction coordinate.

The ideas described served as a basis for the interpretation of the results obtained in the ozonisation of the unsaturated polymers obtained by vulcanising the *cis*- and *trans*-isomers of raw rubbers[68,128]; stretching stresses did indeed increase the rate of ozonisation of *trans*-1,4-polybutadiene, inhibited the ozonisation of *cis*-1,4-polyisoprene (for degrees of deformation exceeding 20%), and did not change the rate of reaction involving 1,2-polybutadiene in which the double bond is localised in a side group. From the standpoint considered here, the authors[68,128] proposed a new explanation for the existence of a critical deformation in the ozone-induced cracking of stressed cured rubbers, which had been known a long time but had not found an adequate interpretation. In the oxidation of elastomers, oxygen-containing functional groups accumulate in the latter and their decomposition is activated in the statically deformed cured rubbers[41].

The data presented in this review show that mechanical stresses interfere with the chain oxidation process at all its stages and can alter significantly the kinetics and even the regime of the oxidative degradation. Mechanical stresses can also lead to a very pronounced spatial localisation of the oxidation process in polymer specimens. They are frequently frozen in the material during its conversion into the finished article, are generated in the article during its use, and finally arise in the ageing process when the latter takes place in a diffusion regime. The oxidation of specimens uniformly throughout their bulk under real conditions is apparently more likely to be the exception rather than the rule. This poses new problems for investigators concerned with its prediction of the durabilities of polymer articles under real operating conditions, because the methods of homogeneous kinetics are inapplicable in this instance.

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Phosphorylated Derivatives of Alkaloids and Nitrogen-containing Heterocycles—Cholinesterase Inhibitors

A.S.Sadykov, D.N.Dalimov, and N.N.Godovikov

The review deals with the synthesis and anticholinesterase activities of phosphorylated derivatives of certain alkaloids and nitrogen-containing heterocycles. It is shown that the conformational properties of the alkaloid and nitrogen-containing heterocycle residues in the composition of the organophosphorus inhibitor (OPI) molecule play an important role in the inhibition of the catalytic activity of cholinesterases. The type of inhibition of cholinesterases also varies as a function of chemical structure.
The bibliography includes 45 references.

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I. INTRODUCTION

A characteristic feature of many esters of quinquevalent phosphorus acids is the ability to inhibit irreversibly cholinesterases. This process is known to proceed via two main stages: the sorption of the inhibitor on the active surface of the enzyme and phosphorylation of this centre. The capacity of an organophosphorus inhibitor (OPI) for sorption on the active surfaces of cholinesterases depends on the presence in their molecules of onium, dipolar, and hydrophobic groups. The second stage of the inhibition process is determined by the electrophilic phosphorylating capacity of the OPI, which depends on the character of the substituents linked to the phosphorus atom[1-14].

The majority of investigators of the relation between the structure of OPI and their anticholinesterase activity have concentrated their attention on the electrophilic phosphorylating capacity of these substances. Many attempts have been made to find a relation between the electrophilic phosphorylating capacity of OPI and their anticholinesterase properties. For example, relations have been sought between the hydrolysability of OPI, the inhibitor concentrations which reduce the activity of cholinesterases by 50% (I_{50}), and the inhibition rate constants k_2, on the one hand, and the Hammett (σ), Taft (σ^*), and Kabachnik (σ^{ph}) constants, on the other. However, only in a few instances has a direct relation been observed between these parameters[1-13].

It has been shown in studies by Kabachnik, Brestkin, Michelson, Rozengart, Godovikov, and co-workers[15-17] that the hydrophobic interactions of the OPI with the active surface of the enzyme play a decisive role in the inhibition of cholinesterases by OPI. However, hitherto no account has been taken of the role of the OPI conformation in their interaction with cholinesterases. Sadykov and co-workers have therefore undertaken studies on the synthesis and anticholinesterase activities of organophosphorus compounds containing alkaloid residues. Since alkaloids can exist in various stable conformations, this made it possible to estimate the influence of the conformations of OPI on their ability to inhibit cholinesterases.

II. SYNTHESIS

In order to be able to investigate the questions raised above, phosphorylated derivatives of alkaloids and nitrogen-containing heterocycles with a logically varied structure were synthesised and their anticholinesterase activities were investigated. Phosphorylated lupinine, epilupinine, anabasine, cytisine, decahydroquinoline, tetrahydroquinoline, 8-hydroxyquinoline, α-, β-, and γ-pipecolines, 2,6-dimethylpiperidine, piperidine, and morpholine were chosen as objects of the investigation. These substances were synthesised by standard methods (see Schemes 1-3).[18-25]

The corresponding methiodides of the majority of these compounds were obtained. The physicochemical constants of the substances synthesised are listed in Tables 1-4.

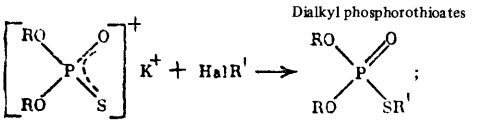
The anticholinesterase activities of the compounds synthesised were determined on enzyme preparations: acetylcholinesterase from human blood erythrocytes with a specific activity 2*E*/mg (EC 3.1.1.7) (ACE) and horse blood serum butyrylcholinesterase with a specific activity of 29*E*/mg (EC 3.1.1.8) (BuCE). The reversible and irreversible inhibiting activities were estimated in terms of the K_i (the reversible inhibition equilibrium constants) and k_2 respectively. These constants were found by standard methods described in the literature[26-28].

III. IRREVERSIBLE INHIBITION OF CHOLINESTERASES

The most characteristic feature of the interaction of OPI with cholinesterases is irreversible inhibition of these enzymes. As a rule phosphorothiolic esters give rise to the irreversible inhibition. A number of dialkyl phosphorothioates containing alkaloid residues in the thioester group were therefore synthesised and their antichlolinesterase activities were investigated.

Thus the study of the anticholinesteras activity of dialkyl phosphorothioates, obtained on the basis of the lupinine and epilupinine alkaloids [(I)-(XIV)] and their methiodides [(I')-(XIV')], showed that all the compounds

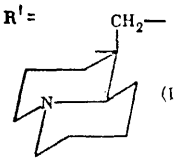
Scheme 1



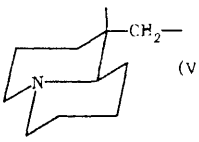
(I)-(XXXIII)

R = C_2H_5; n-C_3H_7; n-C_4H_9; n-C_5H_{11}; iso-C_3H_7; iso-C_4H_9; iso-C_5H_{11};

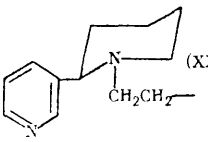
R' =



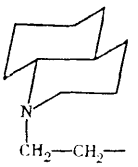
(I)-(VII);



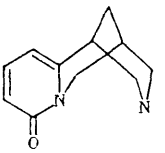
(VIII)-(XIV);



(XXII)-(XXVIII);



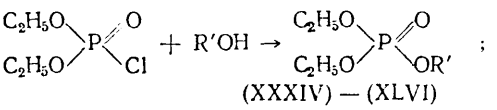
(XV)-(XXI);



(XXIX)-(XXXIII)

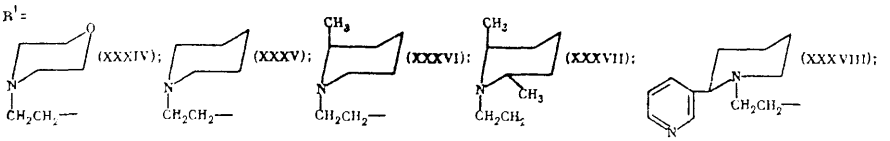
Scheme 2

Diethyl phosphates

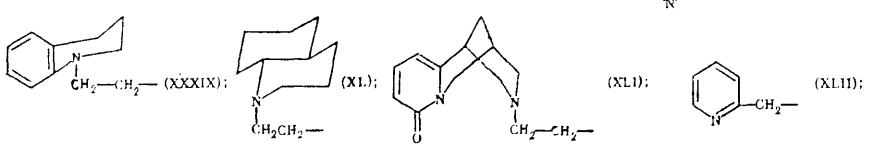


(XXXIV) — (XLVI)

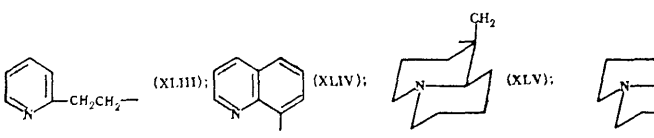
R' =



(XXXIV); (XXXV); (XXXVI); (XXXVII); (XXXVIII);



(XXXIX); (XL); (XLI); (XLII);

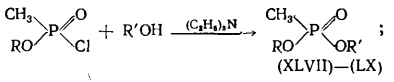


(XLIII); (XLIV); (XLV); (XLVI).

are powerful irreversible inhibitors of cholinesterases[29,30]. Tables 5 and 6 show that an increase in the length of the straight-chain alkyl groups from ethyl to n-pentyl in a series of both types of OPI [(I)-(XIV)] leads to an enhancement of the anticholinesterase activity in relation to acetylcholinesterase (by factor of 27 and 90 for lupinine and epilupinine derivatives respectively). This shows that the dependence of the inhibiting activity on the length of the alkyl groups in O,O-dialky *S*-lupinanyl phosphorothioates is weaker than for the analogous epilupinine derivatives.

Scheme 3

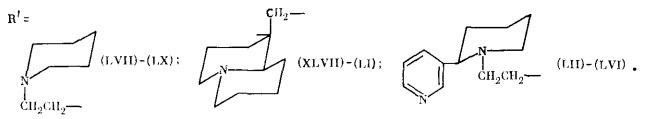
O, Dialkyl methylphosphonates



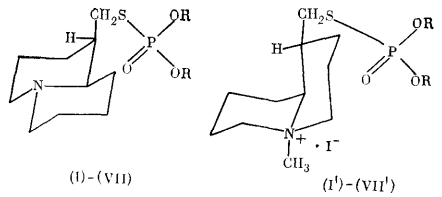
(XLVII)—(LX)

R=C_3H_7—C_6H_{13}; $CH_3O(CH_2)_n$; $C_2H_5O(CH_2)_n$;
$n = 2$—5

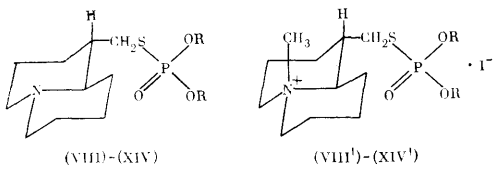
R' =



(LVII)-(LX); (XLVII)-(LII); (LII)-(LVI).



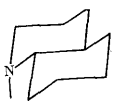
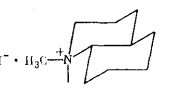
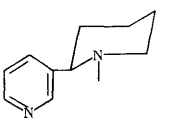
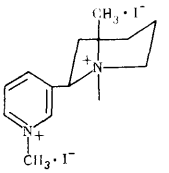
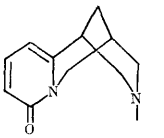
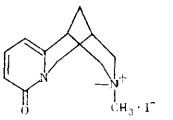
(I)-(VII) (I')-(VII')



(VIII)-(XIV) (VIII')-(XIV')

Similar changes in k_2 as a function of the length of the alkyl moieties of the alkoxy-groups are observed also for the corresponding methiodides (I')-(XIV'). Comparison of the inhibiting activities of the bases (I)-(XIV) with those of their methiodides (I')-(XIV') shows that the values of k_2 for all the methiodides are higher by a factor of 2-8 than for their uncharged analogues. Such a comparatively small increase of the anticholinesterase activity of the methiodides is explained by the fact that at pH 7.5 used in the experiments these compounds are largely protonated[29].

Table 2. *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]bases (XV)-(XXXIII) and their methiodides (XV')-(XXXIII').[21,23]

Compound	R	R'	n_D^{20}	M.p., °C	Yield, %
(XV)	C_2H_5		1.5020		71
(XVI)	n-C_3H_7		1.4931	—	53
(XVII)	n-C_4H_9		1.4950	—	76
(XVIII)	n-C_5H_{11}		1.4919	—	69
(XIX)	iso-C_3H_7		1.4900	—	75
(XX)	iso-C_4H_9		1.4938	—	81
(XXI)	iso-C_5H_{11}		1.4887	—	67
(XV')	C_2H_5		—	101	—
(XVI')	n-C_3H_7		—	94	75
(XVII')	n-C_4H_9		—	117	81
(XVIII')	n-C_5H_{11}		—	110	53
(XIX')	iso-C_3H_7		—	113	77
(XX')	iso-C_4H_9		—	87	83
(XXI')	iso-C_5H_{11}		—	127	61
(XXII)	C_2H_5		1.5201	—	59
(XXIII)	n-C_3H_7		1.5156	—	65
(XXIV)	n-C_4H_9		1.5001	—	68
(XXV)	n-C_5H_{11}		1.4982	—	65
(XXVI)	iso-C_3H_7		1.5112	—	74
(XXVII)	iso-C_4H_9		1.5061	—	66
(XXVIII)	iso-C_5H_{11}		1.5027	—	58
(XXII')	C_2H_5		—	104	54
(XXIII')	n-C_3H_7		—	117	65
(XXIV')	n-C_4H_9		—	121	77
(XXV')	n-C_5H_{11}		—	*	69
(XXVI')	iso-C_3H_7		—	*	49
(XXVII')	iso-C_4H_9		—	*	61
(XXVIII')	iso-C_5H_{11}		—	*	55
(XXIX)	C_2H_5		1.5245	—	51
(XXX)	n-C_3H_7		1.5203	—	67
(XXXI)	n-C_4H_9		1.5186	—	62
(XXXII)	n-C_5H_{11}		1.5162	—	76
(XXXIII)	iso-C_3H_7		1.5234	—	71
(XXIX')	C_2H_5		—	96	70
(XXX')	n-C_3H_7		—	109	62
(XXXI')	n-C_4H_9		—	115	75
(XXXII')	n-C_5H_{11}		—	141	59
(XXXIII')	iso-C_3H_7		—	123	51

* Oily product.

Table 1. *O,O*-Dialkyl *S*-lupinanyl phosphorothioates (I)-(VII), *O,O*-dialkyl *S*-epilupinanyl phosphorothioates (VIII)-(XIV), and their methiodides (I')-(VII') and (VIII')-(XIV').[20,22,24]

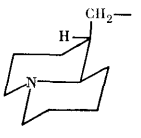
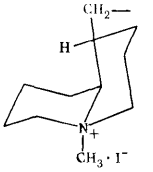
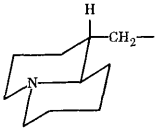
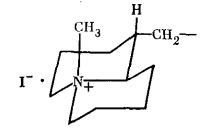
Compound	R	R'	n_D^{20}	$[\alpha]_D^{20}$	Compound	Methiodides		
						R'	m.p., °C	yield, %
(I)	C_2H_5		1.4911	—19.15	(I')		127	90
(II)	n-C_3H_7		1.4961	—24.10	(II')		107	87
(III)	n-C_4H_9		1.4921	—16.42	(III')		102	20
(IV)	n-C_5H_{11}		1.4902	—18.44	(IV')		114	69
(V)	iso-C_3H_7		1.4944	—9.25	(V')		120	84
(VI)	iso-C_4H_9		1.4911	—26.03	(VI')		111	75
(VII)	iso-C_5H_{11}		1.4890	—14.49	(VII')		107	63
(VIII)	C_2H_5		1.4950	+94.53	(VIII')		131	83
(IX)	n-C_3H_7		1.4981	+66.08	(IX')		103	67
(X)	n-C_4H_9		1.5005	+29.64	(X')		133	78
(XI)	n-C_5H_{11}		1.4853	+54.65	(XI')		96	59
(XII)	iso-C_3H_7		1.4943	+75.34	(XII')		137	64
(XIII)	iso-C_4H_9		1.4907	+78.06	(XIII')		119	58
(XIV)	iso-C_5H_{11}		1.4920	+70.40	(XIV')		105	70

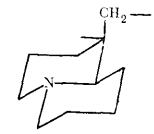
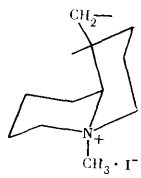
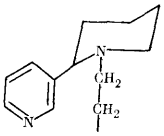
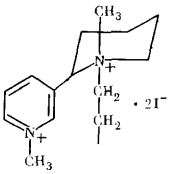
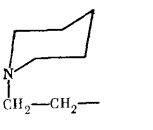
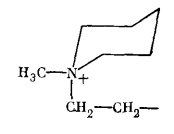
Table 3. Alkyl diethyl phosphates (XXIV)-(XLVI).[25]

Compound	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield, %	M.p., °C
(XXXIV)	1.4500	1.1354	63.22	63.76	74	155—156
(XXXV)	1.4512	1.0565	67.03	66.73	71	151—153
(XXXVI)	1.4507	1.0519	71.34	71.35	64	*
(XXXVII)	1.4765	1.0856	76.16	76.48	58	*
(XXXVIII)	1.4868	1.0935	89.92	90.67	62	103—105
(XXXIX)	1.5210	1.1680	81.59	82.12	87	95—96
(XL)	1.4557	1.0510	82.46	83.01	63	*
(XLI)	1.5547	—	—	—	72	53—55
(XLII)	1.4640	1.0970	61.62	61.26	69	*
(XLIII)	1.4895	1.1273	66.38	65.85	58	*
(XLIV)	1.4075	1.0826	63.95	63.28	83	*
(XLV)	1.4674	1.0848	78.04	78.39	76	*
(XLVI)	1.4560	1.0661	77.80	77.39	78	82—84

Note. MR_D is the molecular refraction, m.p. are the melting points of the methiodides; the yields of the methiodides are nearly quantitative.

* Oily product.

Table 4. Dialkyl methylphosphonates (XLVII)-(LX) and their methiodides (XLVII')-(IX').[17-19]

Compound	R	R'	n_D^{20}	M.p., °C	$[\alpha]_D^{20}$	Yield, %
(XLVII)	$CH_3O(CH_2)_2$		1.5193		13.2	72
(XLVIII)	$C_2H_5O(CH_2)_2$		1.5103	—	12.4	69
(XLIX)	$CH_3O(CH_2)_3$		1.4920	—	20.5	55
(L)	$CH_3O(CH_2)_4$		1.4860	—	20.0	54
(LI)	$CH_3O(CH_2)_5$		1.4842	—	16.0	61
(XLVII')	$CH_3O(CH_2)_2$		—	45—46	—	*
(XLVIII')	$C_2H_5O(CH_2)_2$		—	48—48.5	—	*
(XLIX')	$CH_3O(CH_2)_3$		—	128—129	—	*
(L')	$CH_3O(CH_2)_4$		—	137—138	—	*
(LI')	$CH_3O(CH_2)_5$		—	142—143	—	*
(LII)	$CH_3O(CH_2)_2$		1.5113	—	47.1	68
(LIII)	$C_2H_5O(CH_2)_2$		1.5041	—	44.0	66
(LIV)	$CH_3O(CH_2)_2$		1.4985	—	45.4	56
(LV)	$CH_3O(CH_2)_4$		1.4905	—	40.0	58
(LVI)	$CH_3O(CH_2)_5$		1.4870	—	43.3	54
(LII')	$CH_3O(CH_2)_2$		—	94—95	—	*
(LIII')	$C_2H_5O(CH_2)_2$		—	113—114	—	*
(LIV')	$CH_3O(CH_2)_3$		—	98	—	*
(LV')	$CH_3O(CH_2)_4$		—	104—105	—	*
(LVI')	$CH_3O(CH_2)_5$		—	69—70	—	*
(LVII)	C_3H_7		1.4598	—	—	82
(LVIII)	C_4H_9		1.4632	—	—	76
(LIX)	C_5H_{11}		1.4697	—	—	79
(LX)	C_6H_{13}		1.4711	—	—	68
(LVII')	C_3H_7		—	81—81.5	—	92
(LVIII')	C_4H_9		—	70—71	—	86
(LIX')	C_5H_{11}		—	68—68.5	—	88
(LX')	C_6H_{13}		—	74.5—75.5	—	94

* Nearly quantitative yield.

Tables 5 and 6 and Figs.1 and 2 show that there is a continuous increase of the anticholinesterase activity in relation to ACE of both series of OPI [(I)-(XIV)] with branched hydrocarbon moieties of the alkoxy-groups. A similar behaviour has been noted for the methiodides (I')-(XIV') but with higher constants k_2.

Table 5. The rate constants for the inhibition of ACE and BuCE (k_2, litre mol^{-1} min^{-1}) by *O,O*-dialkyl *S*-lupinanyl phosphorothioates (I)-(VII) and their methiodides (I') to (VII').[29,30]

Compound	R	$10^5 k_2$ (ACE)	$10^7 k_2$ (BuCE)	$\frac{k_2(BuCE)}{k_2(ACE)}$	Compound	$10^5 k_2$ (ACE)	$10^7 k_2$ (BuCE)	$\frac{k_2(BuCE)}{k_2(ACE)}$
(I)	C_2H_5	0.22	2.40	1000	(I')	0.63	4.20	660
(II)	n-C_3H_7	1.50	3.00	200	(II')	5.20	8.40	161
(III)	n-C_4H_9	3.50	59.0	1500	(III')	82.00	90.0	109
(IV)	n-C_5H_{11}	5.80	1.30	224	(IV')	140.0	49.0	35
(V)	iso-C_3H_7	0.10	0.45	450	(V')	0.40	0.92	230
(VI)	iso-C_4H_9	1.60	1.20	75	(VI')	4.90	2.80	56
(VII)	iso-C_5H_{11}	46.0	33	70	(VII')	150	60	40

Table 6. The rate constants for the inhibition of ACE and BuCE (k_2, litre mol^{-1} min^{-1}) by *O,O*-dialkyl *S*-epilupinanyl phosphorothioates (VIII)-(XIV) and their methiodides (VIII')-(XIV').[29,30]

Compound	R	$10^6 k_2$ (ACE)	$10^6 k_2$ (BuCE)	$\frac{k_2(BuCE)}{k_2(ACE)}$	Compound	$10^6 k_2$ (ACE)	$10^7 k_2$ (BuCE)	$\frac{k_2(BuCE)}{k_2(ACE)}$
(VIII)	C_2H_5	0.02	4.80	240	(VIII')	0.16	1.30	81
(IX)	n-C_3H_7	0.38	6.00	16	(IX')	2.80	1.80	6
(X)	n-C_4H_9	1.90	60.0	31	(X')	10.0	7.10	7
(XI)	n-C_5H_{11}	1.80	100.0	55	(XI')	23.0	34.0	15
(XII)	iso-C_3H_7	0.014	3.20	235	(XII')	0.04	0.46	109
(XIII)	iso-C_4H_9	5.40	7.10	1.3	(XIII')	13.0	1.1	9
(XIV)	iso-C_5H_{11}	7.10	47.0	6	(XIV')	16.0	10.0	6

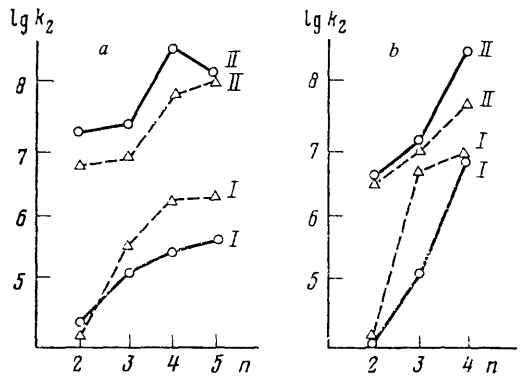


Figure 1. Dependence of $\lg k_2$ on the number n and degree of branching of carbon atoms in the alkyl moiety of the alkoxy-groups in the inhibition of ACE (continuous line I) and BuCE (continuous line II) by *O,O*-dialkyl *S*-lupinanyl phosphorothioates and in the inhibition of ACE (dashed line I) and BuCE (dashed line II) by *O,O*-dialkyl *S*-epilupinanyl phosphorothioates[29]; *a*) OPI with straight-chain alkyl groups; *b*) OPI with isoalkoxy-groups.

The greater inhibiting activity of these compounds in relation to BuCE than ACE is probably a consequence of the improved conditions for the hydrophobic sorption of the alkoxy-groups on the corresponding hydrophobic sections of BuCE. This effect is not associated with the inductive influence of the alkoxy-groups, since the pK_a of the corresponding tautomeric acids are very similar. The constants k_2 for the methiodides (I')-(XIV') in relation to BuCE are only slightly higher (by a factor of 1.5–3) compared with the k_2 for the bases (I)-(XIV).[29,30]

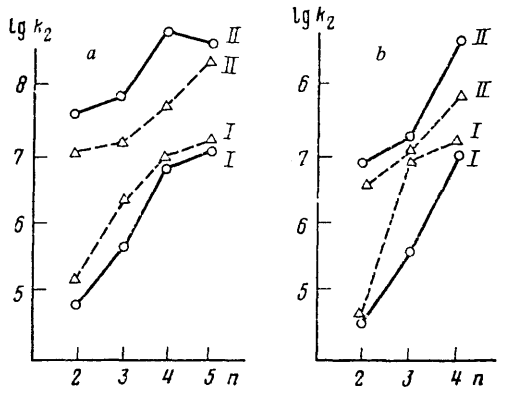
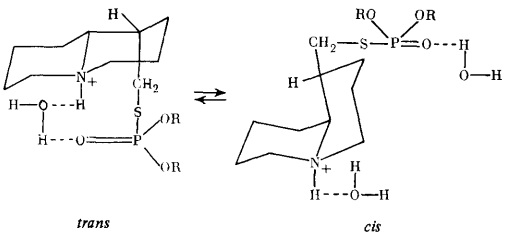


Figure 2. Dependence of lg k_2 on the number n and degree of branching of the carbon atoms in the alkyl moiety of the alkoxy-groups in the inhibition of ACE (continuous line I) and BuCE (continuous line II) by the methiodides of *O,O*-dialkyl *S*-lupinanyl phosphorothioates and in the inhibition of ACE (dashed line I) and BuCE (dashed line II) by the methiodides of *O,O*-dialkyl *S*-epilupinanyl phosphorothioates[29]: *a*) OPI with normal alkoxy-groups; *b*) OPI with isoalkoxy-groups.

Comparison of the anticholinesterase activities of the OPI investigated in relation to ACE and BuCE is of definite interest. In comparing the data obtained for ACE and BuCE, one may note that the ability of both series of OPI [(I)-(XIV)] and their methiodides [(I')-(XIV')] to inhibit BuCE depends more on the length of the alkyl moieties of the alkoxy-groups than in the case of ACE. On the other hand, the appearance of an onium group in the OPI molecule results in a sharp increase of the inhibiting activity in relation to ACE. These data emphasise yet again the tendencies of BuCE and ACE to undergo hydrophobic and ion-ion interactions respectively[15]. All the compounds investigated exhibited selectivity in their activity in relation to BuCE. For the lupinine derivatives (I)-(VII), this effect is very marked and the greatest selectivity is shown by compounds with ethyl (by a factor of 1000), n-butyl (by a factor of 1500), and isopropyl (by a factor of 450) moieties in the alkoxy-groups. On the other hand, in the analogous epilupinine compounds (VIII)-(XIV) this effect is pronounced only for the ethyl (by a factor of 240) and isopropyl (by a factor of 235) derivatives.

Comparison of the inhibiting activities in relation to ACE of the epilupinine derivaties (VIII)-(XIV) with those of the lupinine derivates (I)-(VII) showed that the OPI of the (VIII)-(XIV) series exhibit a more powerful anticholinesterase activity than the analogous compounds of type (I)-(VII). The opposite dependence on the structure of the part of the OPI molecule which is split off is observed on comparing the anticholinesterase activities of the same series of compounds with one another in the inhibition of BuCE. Consequently *O,O*-dialkyl *S*-lupinanyl phosphorothioates and their methiodides exhibit a greater selectivity in their activity in relation to BuCE than their epilupinine analogues. Such specificity in the activity of lupinine derivatives is apparently associated with the fact that in solution the protonated form of the luipinine residue exists mainly in two conformational states: one having a *trans*-junction with the quinolizidine ring and an axial hydroxymethyl group and the other having a *cis*-junction with the quinolizidine ring and an equatorial hydroxymethyl group[31,32]. It may be that the *cis*-conformer is better adapted to sorption on the anionic centre of BuCE; as a result of such sorption, the equilibrium between the *trans*- and *cis*-forms shifts towards the formation of the latter, as a result of which one observes the specificity of the activity of the lupinine derivatives in relation to BuCE.



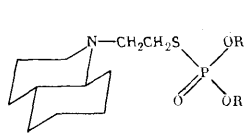
The fact that the methiodides of *O,O*-dialkyl *S*-lupinanyl phosphorothioates, which are known to have a *cis*-junction with the quinolizidine ring of the lupinine fragment and an equatorial thiophosphoryl group, exhibit an analogous specificity in their activity in relation to BuCE may serve as confirmation of the foregoing observations.

The *trans*-quinolizidine ring of the epilupinine derivatives remains unchanged on protonation or conversion into the methiodide and apparently approaches more closely the anionic centre of ACE. This results in a higher activity in relation to ACE.[33]

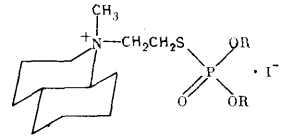
Thus one may note that the very high specificity of the activity of *O,O*-dialkyl *S*-lupinanyl phosphorothioates, and their methiodides is determined by the overall effect of the correspondence to the active centre of BuCE of the alkoxy-groups of the OPI molecule, on the one hand, and of the lupinine fragment on the other. The higher specificity of the activity of the epilupinine derivatives in relation to ACE compared with the lupinine derivatives is in all probability associated with the more effective sorption of the *trans*-quinolizidine ring of the epilupinine residue by the anionic centre of ACE rather than the *cis*-form of the quinolizidine ring in the lupinine derivatives.

As shown above, the inhibiting activities of compounds containing the lupinine and epilupinine derivatives depend significantly on the conformations of these fragments.

The anticholinesterase activitives of *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]decahydroquinolines (XV)-(XXI) and their methiodides (XV')-(XXI') have been investigated; here the decahydroquinoline residue has a structure similar to those of the lupinine and epilupinine residues, but the nitrogen atom is located in one of the rings and not between two rings[33,34].



(XV)-(XXI)



(XV')-(XXI')

All the compounds investigated proved to be inhibitors of cholinesterases with an irreversible type of activity (Table 7). Table 7 shows that decahydroquinoline derivatives exhibit a powerful inhibiting activity in relation to ACE and that the length and degree of branching of the alkoxy-group have little influence on the inhibiting activity. Only the di-isopropoxy-derivative, which is less active by approximately two orders of magnitude than the remaining compounds, is an exception. An analogous behaviour has been observed also for the corresponding methiodides (XV')-(XXI').

Table 7. The rate constants for the inhibition of ACE and BuCE (k_2, litre mol^{-1} min^{-1}) by *N*-[β-(dialkoxyphosphinyl)-mercaptoethyl]decahydroquinolines (XV)-(XXI) and their methiodides (XV')-(XXI').[33,34]

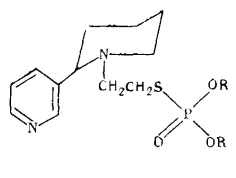
Compound	R	$10^7 k_2$ (ACE)	$10^7 k_2$ (BuCE)	$\frac{k_2(\text{BuCE})}{k_2(\text{ACE})}$	Compound	$10^7 k_2$ (ACE)	$10^7 k_2$ (BuCE)	$\frac{k_2(\text{BuCE})}{k_2(\text{ACE})}$
(XV)	C_2H_5	1.3	0.98	7	(XV')	0.55	2.1	4.1
(XVI)	n-C_3H_7	2.3	1.0	4	(XVI')	1.0	3.4	3.0
(XVII)	n-C_4H_9	4.5	3.6	8	(XVII')	3.3	9.0	3.0
(XVIII)	n-C_5H_{11}	2.7	3.5	13	(XVIII')	2.2	11.0	5.0
(XIX)	iso-C_3H_7	0.021	1.2	582	(XIX')	0.015	3.9	260
(XX)	iso-C_4H_9	2.4	26	100	(XX')	2.7	81	30
(XXI)	iso-C_5H_{11}	6.5	42	64	(XXI')	5.0	93	18.6

N-[β-(dialkoxyphosphinyl)mercaptoethyl]decahydroquinolines are more active in relation to BuCE than ACE. The dependence of the inhibiting activity on the length of straight-chain alkyl groups leads to a sharp increase of the anticholinesterase activity. An analogous behaviour has been observed also for the methiodides. It is noteworthy that the greatest selectivity in their activity is shown by the di-isoalkoxy-derivatives (by a factor of 582 for the di-isopropoxy-derivative, by a factor of 100 for the di-isobutoxy-derivative, and by a factor of 64 for the di-isopentoxy-derivative)[33]. Comparison of the anticholinesterase activities of the decahydroquinoline derivatives with those of the corresponding dialkyl phosphorothioates derived from lupinine and epilupinine shows that *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]decahydroquinolines are stronger inhibitors in relation to ACE than *O,O*-dialkyl *S*-lupinanyl phosphorothioates. This difference between the inhibiting activities can apparently be accounted for by the difference between the structures and conformational states of the decahydroquinoline (*trans*) and lupinine (*cis*) residues. In relation to BuCE, the inhibiting activity of the decahydroquinoline derivatives with straight-chain alkoxy-groups is inferior to that of the analogous lupinine compounds. The opposite is observed in the series of OPI with isoalkoxy-groups[34].

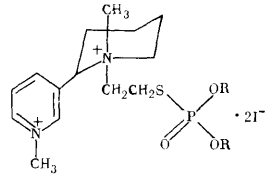
Comparison of the constants k_2 for *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]decahydroquinolines with those of the corresponding *O,O*-dialkyl *S*-epilupinanyl phosphorothioates shows that the anticholinesterase activities of both types of compounds (except the diethoxy- and di-isopropoxy-derivatives) in relation to ACE differ little. However, the methiodides of the decahydroquinoline derivatives are stronger ACE inhibitors than the OPI with the epilupinine fragment. This is apparently associated with the different basicities of the decahydroquinoline and epilupinine residues. *N*-[β-di-isoalkoxyphosphinyl)mercaptoethyl]decahydroquinolines are more active in relation to BuCE than the corresponding *O,O*-di-isoalkyl *S*-epilupinanyl phosphorothioates[33,34].

Thus the introduction of the bulky decahydroquinoline group in the β-position of the thioester group of the OPI instead of the lupinine and epilupinine groups led to a significant alteration of the inhibiting activity in relation to both types of cholinesterases. Comparison of the anticholinesterase properties of the decahydroquinoline derivatives with those of the dialkyl phosphorothioates derived from lupinine and epilupinine demonstrated yet again the sensitivity of the anionic centre of ACE to transoid saturated bicyclic systems. The change in the position of the nitrogen atom in the bicyclic system enhances the inhibiting activity in relation to ACE.

Whereas OPI containing residues of mononitrogen bases in the component which is split off were discussed above, we shall now deal with the anticholinesterase properties of the OPI containing the residue of the alkaloid anabasine [α-(β-piperidinyl)pyridine] in the β-position of the thioesters group and shall compare the data obtained with the inhibiting activities of the analogous decahydroquinoline derivatives[35].



(XXII)-(XXVIII)



(XXII')-(XXVIII')

All the compounds investigated proved to be irreversible cholinesterase inhibitors (Table 8).

Table 8. The rate constants for the inhibition of ACE and BuCE (k_2, litre mol^{-1} min^{-1}) by *N*-[β-dialkoxyphosphinyl)-mercaptoethyl]anabasines (XXII)-(XXVIII) and their methiodides (XXII')-(XXVIII').[35]

Compound	R	$10^5 k_2$ (ACE)	$10^6 k_2$ (BuCE)	$\frac{k_2(\text{BuCE})}{k_2(\text{ACE})}$	Compound	$10^6 k_2$ (ACE)	$10^7 k_2$ (BuCE)	$\frac{k_2(\text{BuCE})}{k_2(\text{ACE})}$
(XXII)	C_2H_5	1.3	0.8	6	(XXII')	0.39	0.15	4
(XXIII)	n-C_3H_7	7.4	2.4	3.5	(XXIII')	3.6	0.53	1.5
(XXIV)	n-C_4H_9	35	7.1	2	(XXIV')	14	2.5	2
(XXV)	n-C_5H_{11}	10	7.7	7	(XXV')	15	4.9	3
(XXVI)	iso-C_3H_7	0.53	4.9	93.7	(XXVI')	0.5	1.3	24
(XXVII)	iso-C_4H_9	18	10	5.5	(XXVII')	33	6.2	2
(XXVIII)	iso-C_5H_{11}	47	90	2	(XXVIII')	50	1.1	0.22

The irreversible inhibiting activity of *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]anabasines in relation to ACE increases with increase of the length of the alkyl groups from ethyl to n-butyl. On further increase in their length, the activity falls.

The irreversible inhibiting activity of *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]anabasines in relation to BuCE is higher than in relation to ACE. These differences depend to a

large extent on the length and degree of branching of the alkoxy-groups. The smallest difference is observed for the dibutyl derivatives (by a factor of two) and the highest for the di-isopropyl derivative (by a factor of 93).[17,35]

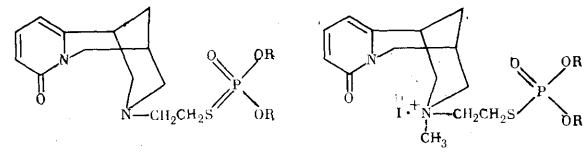
Thus the appearance of a second nitrogen-containing group in the thioester group of the OPI which is to be eliminated has a major influence on the anticholinesterase activity in the case of BuCE. This influence is determined to a large extent by the character of the hydrophobic alkyl moieties of the alkoxy-groups sorbed on the hydrophobic sections of the active surface of the enzyme in the region of the esterase centre.

One may conclude that the presence of two nitrogen-groups in the leaving part of the OPI molecule, which exists largely in the protonated form under the experimental conditions (pH 7.5), impairs the conditions for the hydrophobic sorption of the inhibitor; the alkoxy- and onium groups have a non-concerted influence, which decreases the inhibiting activity [35,36].

The compounds of the onium type which have been investigated show very slight differences in the inhibition of ACE and BuCE, the activities of the majority of them being similar in relation to both enzymes with the exception of the diazopropyl derivative, whose activity is selective in relation to BuCE, and the di-isopentyl derivative, which tends to be more active in relation to ACE (Table 8).[35]

Comparison of the anticholinesterase activities of the *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]anabasines with those of the *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]-decahydroquinolines investigated previously showed that the dialkyl phosphonothioates containing the anabasine group have an only slightly weaker inhibiting activity in relation to ACE than the analogous decahydroquinoline derivatives. *N*-[β-(Diethoxyphosphinyl)mercaptoethyl anabasine, whose anticholinesterase activity is inferior to that of *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]decahydroquinoline by a factor of 10 and the activity of the corresponding methiodide is lower by a factor of 14, is an exception. The different sorbabilities on the anionic centre of ACE of the leaving components of the OPI compared probably have an effect in this instance. The fact that a further increase of the length of the alkoxy-groups smoothes out the differences between the inhibiting activities of decahydroquinoline and anabasine derivatives is apparently associated with the possibility that in the case of the decahydroquinoline analogues there may be an effect of the "non-concerted" sorption on the active surface of ACE,[36] as a result of which small differences between the constants k_2 are observed for these compounds as a function of the length and degree of branching of the alkyl moieties of the alkoxy-groups (by a factor of 2–4). However, since the anabasine fragment of the OPI molecule is less effectively sorbed on the anionic centre of ACE than the decahydroquinoline fragment, they may exhibit a tendency towards an increase of the anticholinesterase activity as a function of the length and degree of branching of the alkyl moieties of the alkoxy-groups (the activity increases by a factor of 30 on passing from C_2H_5 to C_4H_9). The slight differences between the inhibiting activities of the OPI of the two types (with the exception of the diethoxy-analogues) are associated with the increase in the length and the degree of branching of the alkoxy-groups, on the one hand, and with the difference between the structures of the alkanethiol components, on the other. Changes in the phosphoryl component of the molecules of *N*-[β-(diethoxyphosphinyl)mercaptoethyl]anabasines enhance the possibility of "productive" sorption, while similar changes in *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]decahydroquinolines lead to an enhancement of the "unproductive" sorption on the active centre of acetylcholinesterase[17,33,35].

Comparison of the anticholinesterase properties of dialkyl phosphorothioates derived from anabasine with the analogous decahydroquinoline compounds in relation to BuCE shows that the activities of *N*-[β-(diethyoxyphosphinyl)mercaptoethyl]-anabasine and its methiodide are inferior (by a factor of 12 to 13) to those of the analogous decahydroquinoline derivatives. In all probability, the active centres of both ACE and BuCE respond to the differences between the structures of the leaving components of the molecules of the two types of OPI. An increase in the length of the alkoxy-groups results to some extent in a greater similarity of the inhibiting activities of the compounds compared. However, as for ACE, the anabasine derivatives are 4–5 times less active than the analogous dialkyl phosphorothioates derived from decahydroquinoline. Thus the appearance of a second nitrogen-containing group in the leading moiety of the OPI molecule influences the activity in relation to BuCE more than in relation to ACE. It was of interest to follow the variation of the anticholinesterase activities of *N*-[β-(dialkoxyphosphinyl)-mercaptoethyl] cytisines (XXIX)–(XXXIII) and their methiodides (XXIX′)–(XXXIII′), in which the conformational state of the cytisine residue differs sharply from those of lupinine, epilupinine, decahydroquinoline, and anabasine[37].



(XXIX)–(XXXIII) (XXIX′)–(XXXIII′)

Table 9 shows that all the compounds investigated proved to be inhibitors with a combined type of activity†. In relation to ACE, the irreversible inhibiting capacity increases with increase in the length of the alkyl groups up to the n-butyl derivative, after which there is a fall. The replacement of straight-chain alkyl groups by the isopropyl group results in a sharp decrease of the true degree of reversible inhibition of the enzyme by the inhibitor (k_a), which is apparently caused by the inadequate complementarity of the di-isopropoxy-derivative and the ACE active centre[33,37].

Table 9. The rate constants of the inhibition of ACE and BuCE by *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]cytisines (XXIX)–(XXXIII) and their methiodides (XXIX′)–(XXXIII′)* [37]

Compound	R	ACE			BuCE			
		$10^5 k_a$, litre mol^{-1}min^{-1}	$10^{-7} K_{ir}$, mol litre^{-1}	$10^{-7} K_{is}$, mol litre^{-1}	$10^4 k_a$, litre mol^{-1}min^{-1}	$10^{-7} K_{ir}$, mol litre^{-1}	$10^{-7} K_{is}$, mol litre^{-1}	k_a(BuCE)/k_a(ACE)
(XXIX)	C_2H_5	0.63	710	15	0.35	43	5.0	5.5
(XXX)	n-C_3H_7	1.2	9.6	6.5	3.3	3.7	0.18	2.7
(XXXI)	n-C_4H_9	35	1.3	2.3	9.0	4.8	2.1	2.6
(XXXII)	n-C_5H_{11}	74	1.3	4.8	9.6	3.6	5.4	13.2
(XXXIII)	iso-C_3H_7	0.35	12	7.4	5.1	4.6	0.2	145
(XXIX′)	C_2H_5	1.1	66	1.5	0.61	3.1	0.5	5.4
(XXX′)	n-C_3H_7	3.1	6.0	0.21	8.0	0.41	0.62	2.7
(XXXI′)	n-C_4H_9	11.0	2.2	0.21	14	0.15	0.31	1.2
(XXXII′)	n-C_5H_{11}	23	4.5	0.64	17	0.1	0.91	8.2
(XXXIII′)	iso-C_3H_7	0.64	490	0.17	7.0	0.2	0.75	105.9

* For the significance of k_a, K_{ir}, and K_{is}, see Brestkin and Godovikov[36].

† A number of studies, reviewed by Brestkin and Godovikov[36], have been devoted to this type of inhibition.

In relation to BuCE, the test compounds are more active than in relation to ACE. An increase in the length of the alkyl moieties of the alkoxy-groups increases the inhibiting activity. In contrast to ACE, BuCE is relatively insensitive to the replacement of the straight-chain alkyl groups by the isopropyl group. It is noteworthy that *N*-[β-(di-isopropoxyphosphinyl)mercaptoethyl]cytisine shows the greatest selectivity in relation to BuCE (by a factor of 145). This selectivity is apparently associated with the less effective sorption of the di-isopropoxy-derivative on the active surface of ACE.

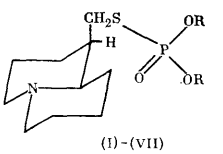
The reversible inhibiting activity in relation to ACE increases on passing from the ethyl to the propyl derivative, but a further increase in the length of the alkyl group has little influence on the reversible inhibiting activity of the organophosphorus compound investigated. It must be emphasised that the reversible inhibitors derived from cytisine exhibit selectivity in their activity with respect to BuCE.

The quaternisation of the nitrogen atom results in a slight increase of the anticholinesterase activity in relation to both enzymes (by a factor of 2–3), but the selectivity in relation to BuCE then falls. It follows from the foregoing that, compared with the previous compounds, *N*-[β-(dialkoxyphosphinyl)mercaptoethyl]cytisines and their methiodides proved to be significatnly weaker inhibitors with irreversible activity. The impairment of the inhibiting activity of cytisine derivatives may be associated with the steric hindrance of the cytisine residue in the sorption of the inhibitor on the active surface of the enzyme[37].

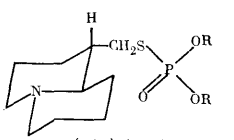
IV. COMPARISON OF THE ACTIVITIES OF THE OPI DERIVED FROM LUPININE AND EPILUPININE

Tables 10 present data for the effect on the cholinesterases of various species of mammals and arthropods by *O,O*-dialkyl *S*-lupinanyl phosphorothioates and *O,O*-dialkyl S-epilupinanyl phosphorothioates[30,38], which make it possible to discover a number of characteristic features. In the vast majority of cases, the OPI investigated proved to be stronger inhibitors of the ACE from the heads of files than of the mammalian ACE. This applies particularly to the first members of the series of compounds containing both straight-chain and branched groups. For example, the ACE from the heads of flies proved to be 15000 more sensitive to *O,O*-diethyl *S*-lupinanyl phosphorothioate than the ACE from human erythrocytes; the sensitivity in relation to the di-isopropyl derivative of lupinine was higher only by a factor of 250. In the case of epilupinine derivatives, the opposite relation between the sensitivities of the ACE from the heads of flies and human erythrocytes was observed, the increase in sensitivity being greater for the di-isopropyl compound (by a factor of 1000) than for the ethyl compound (by a factor of 550). It is noteworthy that some of the compounds investigated have the unique ability to suppress the ACE from the heads of flies: the absolute bimolecular inhibition rate constants reached approximately 10^8 litre mole^{-1} min^{-1}. An increase in the length of the straight-chain alkyl group in lupinine derivatives appreciably enhanced the anticholinesterase activity in relation to the mammalian enzyme. In contrast to this, the sensitivity of the ACE from the heads of flies to the OPI fell sharply with increase in the length of the alkyl group. Thus the compound with the C_5H_{11} group proved to be 120 times less active than the ethyl derivative. An increase in the length of the iso-groups increased the ability to suppress the mammalian ACE but had virtually no influence on the ACE from the heads of flies. In epilupinine derivatives an increase in the length of the straight-chain alkyl group had a very insignificant and indefinite influence on their ability to inhibit the ACE from the heads of flies. Indeed, the effect of epilupinine derivatives on the mammalian ACE did not differ from that of the analogous lupinine compounds. With increase in the length of both straight-chain and branched alkyl groups, the anticholinesterase activity increased significantly. This was manifested most clearly in relation to the ACE from human blood erythrocytes: on passing from C_2H_5 to C_5H_{11}, the activity increased by a factor of 90 and on passing from iso-C_3H_7 to iso-C_5H_{11} the activity rose by a factor greater than 500. The facts enumerated above indicate significant differences between the structures of the active surfaces of the cholinesterases from mammals and flies. It has been noted[39] that in the insect cholinesterase the distance between the anionic and esterase centres is greater than in the mammalian cholinesterase. However, it is difficult to account for the data obtained in terms of these differences alone. The results showing that the hydrophobic region around the anionic centre in the ACE from the heads of flies is more bulky and wider than in the ACE from human erythrocytes are of great interest. One canot rule out the possibility that this can justify the hypothesis of a greater complementarity between the bulky heterocyclic residue in the OPI investigated and the anionic centre of the fly cholinesterases compared with the mammalian enzyme. The fact that very small conformational differences between lupinine and epilupinine are sufficient to have a pronounced influence on the anticholinesterase effect of the OPI is quite probably also associated with precisely this factor. As regards the sharp decrease of the anticholinesterase activity of the OPI in relation to the ACE from the heads of flies with increase in the length of the hydrocarbon group, there is no doubt whatever that the cause lies in the difference between the hydrophobic environments of the esterase centres in the mammalian and insect enzymes. It may be that on this part of the active surface of the insect enzyme, the hydrophobic regions are not very large and that immediately beyond them there are hydrophilic regions which not only do not promote but actually actively hinder the sorption of large hydrocarbon groups, which leads to a pronounced decrease of the anticholinesterase effect.

Table 10. The rate constants for the inhibition of ACE of different origins (10^5 k_2, litre mol^{-1} min^{-1}) by *O,O*-dialkyl *S*-lupinanyl phosphorothioates (I)-(VII) and *O,O*-dialkyl *S*-epilupinanyl phosphorothioates (VIII)-(XIV).[42]



(I)-(VII)

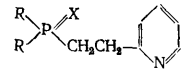


(VIII)-(XIV)

R	(I)–(VII)			(VIII)–(XIV)		
	from mouse brain	from rabbit erythrocytes	from heads of flies	from mouse brain	from rabbit erythrocytes	from heads of flies
C_2H_5	0.21	0.11	3400	0.24	0.77	110
n-C_3H_7	0.36	75	1200	1.4	4.5	190
n-C_4H_9	3.6	25	290	4.1	3.6	17
n-C_5H_{11}	0.12	0.52	28	4.1	3.6	17
iso-C_3H_7	0.002	0.16	25	0.12	0.04	140
iso-C_4H_9	0.28	2.1	120	7.0	1.2	19
iso-C_5H_{11}	3.0	3.8	34	12	6.6	62

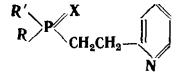
V. REVERSIBLE INHIBITION OF CHOLINESTERASES

The reversible inhibition of the catalytic activity of cholinesterases is less characteristic of organophosphorus inhibitors. The purely reversible inhibition of cholinesterases by organophosphorus compounds was first demonstrated[40] in relation to a series of β-(2-pyridyl)ethylphosphine oxides and sulphides (Table 11).



Subsequently, it was shown that the alkyl esters of quinquevalent phosphorus oxyacids are capable of inhibiting cholinesterases only reversibly[41–44].

Table 11. The rate constants for the reversible inhibition of cholinesterases (K_i, mol litre^{-1}) [40] by the compounds



R	R′	X	K_i, mol litre^{-1}	
			BuCE	ACE
C_2H_5	C_2H_5	O	$2.6\cdot10^{-4}$	$5.0\cdot10^{-4}$
C_2H_5	C_6H_5	O	$2.6\cdot10^{-4}$	$32\cdot10^{-3}$
C_2H_5	C_6H_5	S	$4.2\cdot10^{-5}$	$6.2\cdot10^{-4}$
C_6H_5	C_6H_5	O	$3.7\cdot10^{-5}$	$4.6\cdot10^{-4}$
C_6H_5	C_6H_5	S	$3.6\cdot10^{-6}$	$3.8\cdot10^{-4}$
Pyridine	—	—	$1.2\cdot10^{-2}$	$2.5\cdot10^{-2}$

An analogous effect has been observed for substituted alkyl esters of phosphoric and methylphosphonic acids containing alkaloid and certain heterocyclic residues.

Thus the study of the anticholinesterase activities of diethyl phosphate derivatives of morpholine, piperidine, α-pipecoline, anabasine, tetrahydroquinoline, decahydroquinoline, cytisine, α-hydroxymethylpyridine, α-hydroxyethylpyridine, 8-hydroxyquinoline, lupinine, and epilupinine [compounds (XXIV)–(XLVI) except compound (XXXVII)] showed that all the compounds investigated are competitive reversible inhibitors of ACE (Table 12). The dependence of the inhibiting activity on the structure of the cationic group of the organophosphorus inhibitor appears to be extremely complex. Thus the morpholine derivative does not inhibit the catalytic activity of acetylcholinesterase at all, the inhibiting activity increasing on going over to the piperidine, α-pipecoline, and then anabasine derivatives. However, the condensation of cyclohexane and benzene rings with the piperidine ring (the decahydroquinoline and tetrahydroquinoline derivatives) does not alter significantly the anticholinesterase activity. In all these compounds the nitrogen atom is present in one ring, while its introduction into the position between two rings leads to a decrease of the inhibiting activity of the given substances (the lupinine and epiluinine derivatives). The 8-hydroxyquinoline derivative is the most active inhibitor in this series of substances. Its activity is apparently due to the correspondence of the distances between the phosphorus and nitrogen atoms in the inhibitor and between the carbonyl carbon atom and nitrogen in acetylcholine. Weak inhibiting properties in relation to acetylcholinesterase can apparently be explained by the fact that the phosphate group of the inhibitor is not complementary in relation to the active centre of this enzyme[25].

Table 12. The anticholinesterase properties of the esters of *O,O*-diethylphosphoric acid containing heterocyclic groups[25].

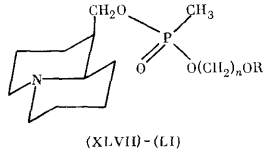
Compound	ACE	BuCE	Compound	ACE	BuCE
	K_i, mol litre^{-1}	K_i, mol litre^{-1}		K_i, mol litre^{-1}	K_i, mol litre^{-1}
(XXXIV)	0	0	(XLII) *	19%	$2.6\cdot10^{-4}$
(XXXV)	$1.15\cdot10^{-3}$	$2.60\cdot10^{-5}$	(XLII) **	$2.50\cdot10^{3}$	$1.4\cdot10^{4}$
(XXXVI) *	27%	$6.70\cdot10^{-5}$	(XLIII) **	$4.90\cdot10^{3}$	$2.9\cdot10^{5}$
(XXXVIII)	$6.60\cdot10^{-4}$	$2.70\cdot10^{-4}$	(XLIV)	$2.60\cdot10^{-4}$	$4.8\cdot10^{-6}$
(XXXIX)	$3.60\cdot10^{-3}$	$6.70\cdot10^{-3}$	(XLV)	$1.15\cdot10^{-3}$	$1.4\cdot10^{-4}$
(XL)	$3.10\cdot10^{-4}$	$7.1\cdot10^{-4}$	(XLVI)	$2.20\cdot10^{-4}$	$1.1\cdot10^{-5}$

*The percentage inhibition at a concentration of 7.2×10^{-3} M is quoted.

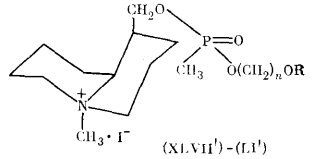
**These substances proved to be irreversible inhibitors and were assessed in terms of the bimolecular interaction constants k_2.

It can be seen from the foregoing that phosphates are very weak reversible inhibitors of both types of enzymes. However, they in fact exhibit a definite selectivity in relation to butyrylcholinesterase. Therefore, bearing in mind that methylphosphoric acid derivatives have a more specific activity in relation to acetylcholinesterase, for which hydrophobic interactions are less typical, the anticholinesterase activities of derivatives of methylphosphonic acids containing a hydrophilic group in the non-leaving part of the molecule and the residues of the alkaloids anabasine, lupinine and piperidine in the leaving group were therefore investigated. It was assumed that the specific structure of the anabasine and lupinine residues, in which there is a considerable hydrophobic environment around the nitrogen atom, promotes the formation of comparatively stable enzyme-inhibitor complexes [17,18].

The study of the inhibiting activities of alkoxyalkyl lupinanyl methylphosphonates (XLVII)–(LI) showed that there is a tendency, albeit small, towards an increase of the inhibiting activity in relation to ACE and BuCE with increase of the length of the alkoxy-group (Table 13, and Fig. 3). [45]



(XLVII)–(LI)



(XLVII′)–(LI′)

There is every reason to suppose that the change in inhibiting activity noted above is associated with an increase of the ability of the OPI to be sorbed on the active surfaces of the enzymes via a hydrophobic mechanism. However, the presence of the hydrophilic oxygen atom in the alkyl moiety in the alkoxy-group hinders this process and thereby reduces the efficiency of the inhibitors.

The methiodides of (*O*-alkoxyalkyl)methylphosphinyllupinines are less active reversible inhibitors of ACE and BuCE than their uncharged analogues. Evidently, the

charge, interacting at the anionic site, does not ensure the most effective hydrophobic sorption (Fig.4). It is of interest to note that the inhibiting activities of both types of compounds depend not only on the distance between the oxygen and phosphorus atoms but also on the position of the former in relation to the alkyl moiety of the alkoxy-group. The presence of the oxygen atom in the β-position in the alkoxy-group to some extent interferes with hydrophobic sorption.

Table 13. The constants for the reversible inhibition of cholinesterases (K_i, mol litre^{-1}) by compounds (XLVII)–(LI) and (XLVII')-(LI'). [45]

Compound	R	n	$10^4 K_i$ (ACE)	$10^4 K_i$ (BuCE)	Compound	$10^3 K_i$ (ACE)	$10^3 K_i$ (BuCE)
(XLVII)	CH_3	2	3.61	2.5	(XLVII')	4.2	1 25
(XLIX)	CH_3	3	2.87	1.2	(XLIX')	1.30	0.72
(L)	CH_3	4	2.02	0.93	(L')	0.74	0.65
(LI)	CH_3	5	1.32	0.53	(LI')	0.63	0.47
(XLVIII)	C_2H_5	2	2.94	1.8	(XLVIII')	2.42	1.04

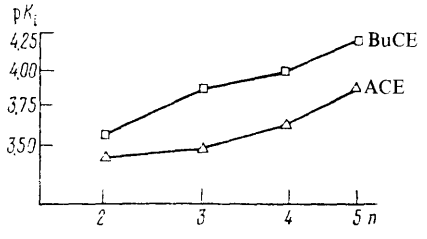


Figure 3. Dependence of the inhibition constant (pK_i) on the length of the alkoxy-group in compounds of type (V). [17,45]

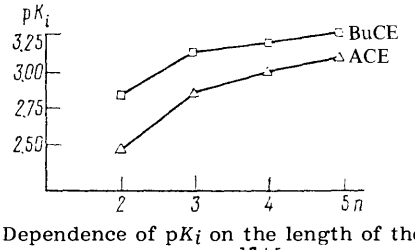
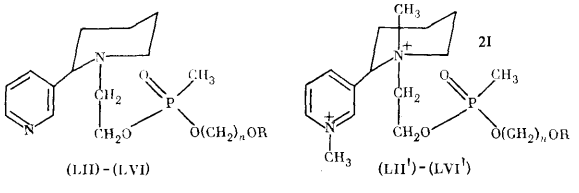


Figure 4. Dependence of pK_i on the length of the alkoxy-group in compounds of type (VI). [17,45]

N-β-(ω-Alkoxyalkoxy)methylphosphinyloxyethylanabasines (LII)–(LVI) and their dimethiodides (LII')–(LVI') proved to be reversible inhibitors with competitive activity[45].



An increase in the length of the alkyl moiety of the alkoxy-group entails a small (three fold) increase of the inhibiting activity in relation to both acetylcholinesterase and butyrylcholinesterase.

An increase in the overall length of the alkoxy-group is accompanied by an increase of the inhibiting activity in relation to both enzymes, which is very low in the case of butyrylcholinesterase and is appreciable in the case of acetylcholinesterase (Table 14, Fig.5).

Table 14. The constants for the reversible inhibition of cholinesterases (K_i, mol litre^{-1}) by N-[β-(ω-alkoxyalkoxy)-methylphosphinyloxyethyl]anabasines (LII)–(LVI) and their methiodides (LII')-(LVI'). [17,45]

Compound	R	n	$10^4 K_i$ (ACE)	$10^4 K_i$ (BuCE)	Compound	$10^4 K_i$ (ACE)	$10^5 K_i$ (BuCE)
(LII)	CH_3	2	9.6	1.88	(LII')	6.4	2.96
(LIV)	CH_3	3	5.4	1.01	(LIV')	3.6	3.08
(LV)	CH_3	4	3.7	0.735	(LV')	3.08	4.6
(LVI)	CH_3	5	2.85	0.545	(LVI')	5.50	2.94
(LIII)	C_2H_5	2	7.62	1.265	(LIII')	4.30	1.24

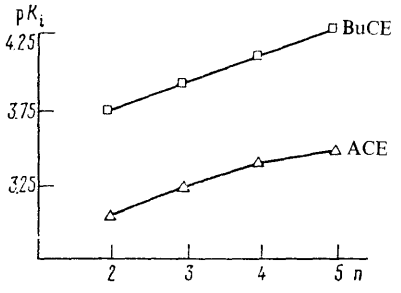


Figure 5. Dependence of pK_i on the length of the alkoxy-group in compounds of type (LII)–(LVI). [17,45]

Table 15. The constants for the reversible inhibition of cholinesterases (K_i, mol litre^{-1}) by N-[β-(alkoxyethyl-phosphinyloxyethyl)piperidines (LVII)–(LX) and their methiodides (LVII')-(LX'). [17,45]

Compound	R	$10^4 K_i$ (ACE)	$10^4 K_i$ (BuCE)	Compound	$10^4 K_i$ (BuCE)
(LVII)	C_3H_7	4.26	1.47	(LVII')	1.32
(LVIII)	C_4H_9	3 21	1.61	(LVIII')	1.05
(LIX)	C_5H_{11}	2.06	1.015	(LIX')	0.677
(LX)	C_6H_{13}	1.55	0.307	(LX')	0.364

N-β-(Alkoxymethylphosphinyloxyethyl)piperidines (LVII)–(LX) are reversible competitive inhibitors of cholinesterases.

The activities of the test compounds in relation to butyrylcholinesterases are inferior to those of analogous anabasine and lupinine derivatives. The average K_i is 1×10^{-4} M, decreasing almost by a factor of 5 in the series of substances investigated (Table 15).

Piperidine derivatives are also weaker inhibitors of acetylcholinesterase than the corresponding anabasine and lupinine derivatives.

The methiodides of *N*-β-(alkoxymethylphosphinyloxyethyl)-piperidines (LVII')-(LX') have the same inhibiting effect on butyrylcholinesterases as their uncharged analogues (Table 15, and Fig.6).

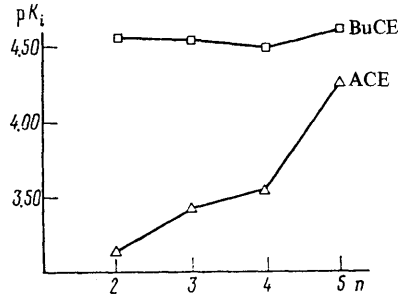


Figure 6. Dependence of pK_i on the length of the alkoxy-group in compounds of type (LVII)-(LX).[17,45]

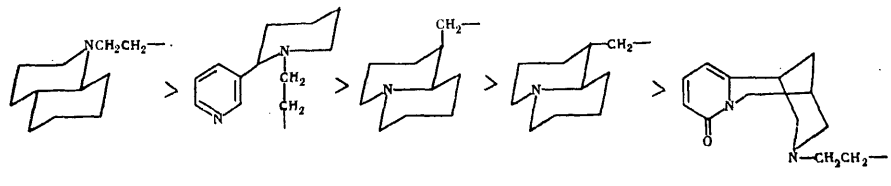
Thus the presence of an oxygen atom in the alkyl moiety of the reversible inhibitors, both with and without positive charges in the molecule, has an appreciable influence on the character of their interaction with cholinesterases. One should note that, for both the lupinine and anabasine derivatives, the characteristics of the changes in the anticholinesterase activity are similar. On this basis, one may conclude that the hydrophilic oxygen atom in the alkoxy-group of the reversible organophosphorus inhibitor in general reduces the inhibiting activity. Furthermore, one should also note that the reversible inhibiting activity depends significantly also on the structure of the heterocyclic residue present in the leaving component of the OPI molecule.

VI. CONCLUSION

Thus, comparison of the anticholinesterase activities of the *O*,*O*-dialkyl phosphorothioates which we investigated, containing the residues of the alkaloids lupinine, epilupinine, anabasine, cytisine, and decahydroquinoline in the alkanethiol component of the organo phosphorus inhibitor, showed that all the compounds exhibit a greater tendency towards interaction with the horse blood serum butyrylcholinesterase than with the acetylcholinesterase from human blood erythrocytes. Similar properties of dialkyl phosphorothioates were known previously but in our studies the selectivity of the activity of the above substances in relation to butyrylcholinesterase depends not only on the structure of the phosphoryl component but also on the bulk and conformational possibilities in the leaving part of the inhibitor molecule. Dialkyl phosphorothioates containing the lupinine residue proved to be more highly specific inhibitors of butyrylcholinesterase than the epilupinine derivatives. Under the same experimental conditions and for identical structures of the phosphoryl component of the lupinine and epilupinine derivatives, the differences between the conformational states of the protonated forms of lupinine and epilupine in solution can be appropriately regarded as the cause of the selectivity of their activity in relation to butyrylcholinesterase[17,37]. The protonated forms of *O*,*O*-dialkyl *S*-lupinanyl phosphorothioates apparently exist in two conformational states, as in the case of acyl-lupinanes: having a *trans*-junction with the quinolizidine ring and an axial hydroxymethyl group and having a *cis*-junction with the quinolizidine ring and an equatorial hydroxymethyl group. These two conformers are in dynamic equilibrium. It may be that the *cis*-conformer is better adapted to sorption on the anionic centre of butyrylcholinesterase, as a result of which the sorption equilibrium is displaced towards the formation of the *cis*-form and this entails the observed specificity of the activity of lupinine derivatives in relation to butyrylcholinesterase. The conformation of the epilupinine derivatives under the experimental conditions at pH 7.5 to 7.8 remains unchanged, i.e. it has a *trans*-junction with the quinolizidine ring and an equatorial hydromethyl group[29,30-33,38].

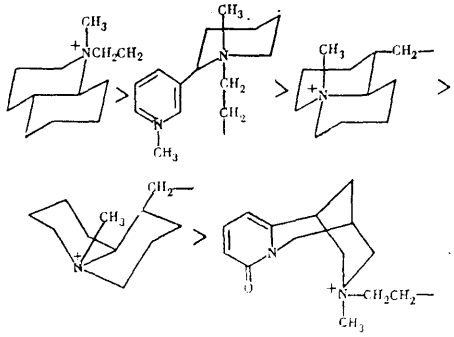
Comparison of the anticholinesterase activities of the diethyl phosphorothioates containing the residues of the above alkaloids as well as cytisine, anabasine, and decahydroquinoline made it possible to set up a series based on the relative inhibiting activities as a function of the structure of the leaving components of the organophosphorus compounds investigated: the constants k_2 in relation to the ACE from the heads of flies are 9.3×10^5 for *N*-[β-(diethoxyphosphinyl)-mercaptoethyl]anabasine, 1.8×10^4 for *N*-[β-(diethoxyphosphinyl)mercaptoethyl]cytisine, and 1.3×10^6 litre mol^{-1} min^{-1} for *N*-[β-(diethoxyphosphinyl)mercaptoethyl]decahydroquinoline. In terms of the strength of the irreversible inhibition of human blood erythrocyte acetylcholinesterase, the inhibitors $(C_2H_5O_2)P(O)SR$ can be arranged in the following sequence as a function of the substituent R:

Scheme 4



On the other hand, the sequence of their methiodides is as follows:

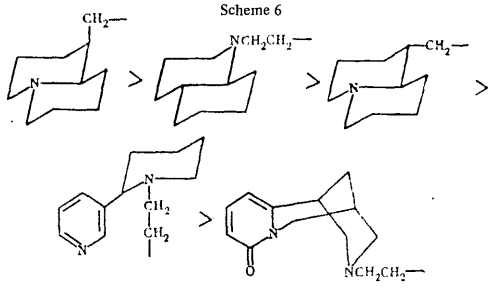
Scheme 5



It is seen from the above sequences that an increase in the complexity of the piperidine ring in the test substances results in a marked decrease of the irreversible inhibiting activity in relation to the erythrocyte acetylcholinesterase, which confirms the existence of a weakly hydrophobic framework around the anionic centre in the acetylcholinesterase from human erythrocytes. In the second sequence the methiodide of *O,O*-diethyl *S*-lupinanyl phosphorthioate is less active than the analogous epilupinine derivative, which is apparently due to the influence of the conformation change in the lupinine derivative on conversion into the methiodide[33].

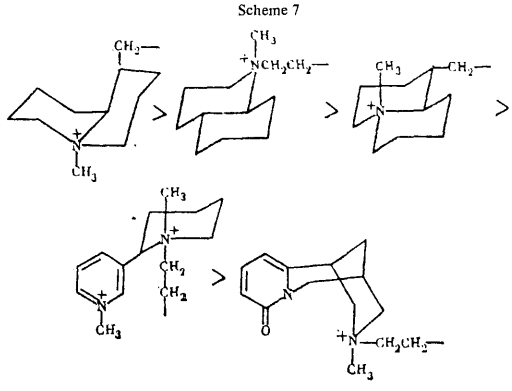
Another picture is observed when the above inhibitors act on butyrylcholinesterase. Butyrylcholinesterase is known to tend to undergo hydrophobic interactions and the hydrophobic framework around the anionic centre in this enzyme is more extensive than in acetylcholinesterase. The given sequence shows that the anionic centre of butyrylcholinesterase has a definite boundary and tends to sorb labile bicyclic systems and transition to systems containing groups such as the pyridine and quinolizidine groups results in a sharp decrease of the reversible inhibiting activity:

Scheme 6



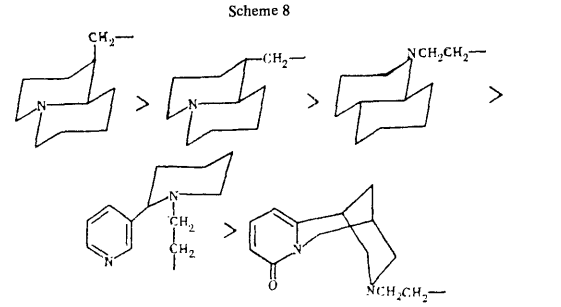
An analogous behaviour has been observed also for the methiodides of the test compounds:

Scheme 7



The compounds investigated proved to be very powerful inhibitors of the cholinesterase from the heads of flies with the exception of the cytisine derivative, which exhibited a very weak inhibiting activity in its interaction with all the enzymes investigated:

Scheme 8



Comparison of these series of relative inhibiting activities of the compounds, namely in their interaction with butyrylcholinesterase, shows that the first four compounds of the last sequence are very powerful inhibitors of both the acetylcholinesterase from the heads of flies and of butyrylcholinesterase. This suggests that in all probability the hydrophobic frameworks around the anionic centres of horse blood serum butyrylcholinesterase and the acetylcholinesterase from the heads of flies have a definite similarity in their steric structures[33].

The study of the acetylcholinesterase activities of *O,O*-dialkyl *S*-lupinanyl phosphorothioates and the corresponding epilupinanyl derivatives with straight-chain substituents in relation to the acetylcholinesterase from the heads of flies showed that the inhibiting activity of the lupinine derivatives decreases sharply with increase in the length of the alkoxy-groups in the inhibitor molecules; an analogous but less marked behaviour has been observed also for the epilupinine derivatives. The hydrophobic component in the region of the esterase centre of the acetylcholinesterase from the heads of flies is apparently small compared with the mammalian enzyme and immediately beyond it there are hydrophilic regions which hinder the sorption of large hydrocarbon groups, reducing the acetylcholinesterase activity. The investigations have yielded data which made it possible to discover differences between the structures of the active centres of mammalian cholinesterases and acetylcholinesterase from the heads of flies.

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Carboxylic Acid Esters as Substrates of Cholinesterases

A.P.Brestkin, E.V.Rozengart, A.A.Abduvakhabov, and A.A.Sadykov

Data on the kinetics of the hydrolysis of various carboxylic acid esters by two main types of cholinesterases—acetylcholinesterase from human erythrocytes and buryrylcholinesterase from horse blood serum—are surveyed. It is shown that the rate of enzyme hydrolysis depends significantly on the structure of the acyl part of the ester molecule, the nature of the ester heteroatom, the structure of the alcohol component, and particularly the structure of the onium group. Esters based on natural products are of special interest as specific substrates of these enzymes. The role of the productive and non-productive sorption of the substrates in enzyme catalysis is demonstrated.
The bibliography includes 81 references.

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I. INTRODUCTION

Cholinesterases (CE) are enzymes which hydrolyse the choline esters of carboxylic acids at a higher rate than non-choline esters. A characteristic feature of these enzymes is the inhibition of their catalytic activity by low concentrations of tetra-alkylammonium compounds, certain organophosphorus compounds, and esters of substituted carbamic acids. The sensitivity to eserine at concentrations of 10^{-5} M and below is believed to be one of the most reliable criteria for the classification of an enzyme as a cholinesterase.

Two main types of cholinesterases have been most thoroughly investigated: acetylcholinesterase (ACE) or acetylcholine acyl-hydrolase (EC 3.1.1.7) and butyrylcholinesterase (BuCE)—a variety of acylcholine acyl-hydrolases (EC 3.1.1.8), which differ in their substrate specificity and sensitivity to various inhibitors. ACE hydrolyses acetylcholine (AC) at the highest rate, propionylcholine (PrC) and acetyl-β-methylcholine (MeC) somewhat more slowly, and has almost no influence on the rate of hydrolysis of butyrylcholine (BuC) and benzoylcholine (BzC). On the other hand, butyrylcholinesterase hydrolyses BuC at the highest rate, PrC, AC, and BzC somewhat more slowly, and does not influence the rate of hydrolysis of MeC. Furthermore, in contrast to BuCE, the catalytic activity of ACE is inhibited by high substrate concentrations.

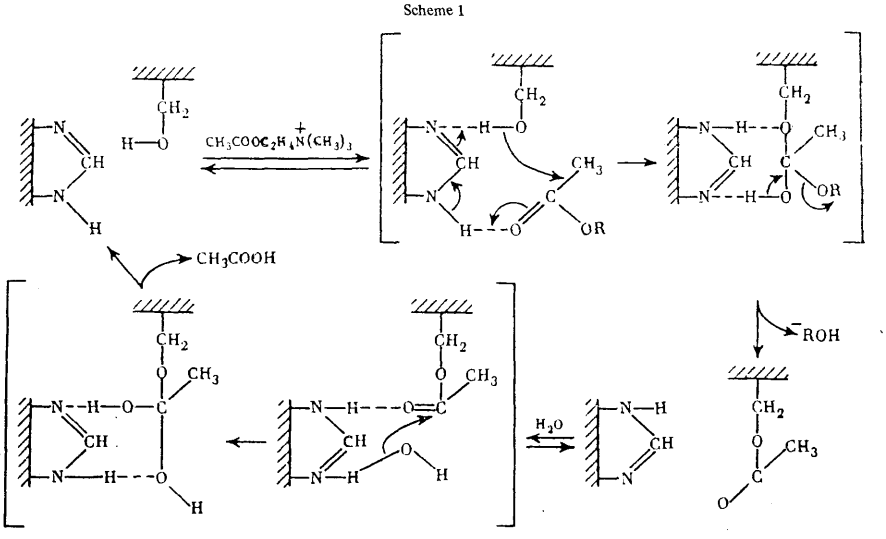
ACE of nerve tissue is directly involved in the transmission of nerve excitation from the nerve to the innervated cell. The biological role of BuCE as well as that of the ACE contained in the erythrocytes of many animals has not been elucidated.

Cholinesterases are the target of the inhibiting activity of certain medicinal preparations, organophosphorus and carbamate insectoacaricides, and organophosphorus poisons.

There exists an extensive literature on cholinesterases, which has been comprehensively surveyed in monographs[1-5] and a number of reviews[6-8].

The extremely high catalytic activity of cholinesterases is due to the unique structure of their active surface. Apart from the esterase site, where the ester linkage is ruptured, at a distance of 4–5 Å from it on the surface there is an anionic site which is responsible for the specific binding of the ammonium group of AC and promotes a favourable orientation of the substrate molecule[2-4]. Apart from Coulombic interaction of the ammonium group with the anionic site of the enzyme, the orientation of substrates and inhibitors is

Scheme 1

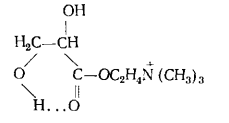


greatly influenced by the hydrophobic interaction of their hydrocarbon groups with the hydrophobic sections located in the region of both the anionic and esterase sites[8].

It is suggested that the anionic site consists of the carboxylate anion derived from the dibasic glutamic or aspartic acid incorporated in the polypeptide chain of the enzyme. The esterase site on the active surface of the enzyme has a more complex structure. The serine hydroxyl, which is acylated on interaction with substrates and phosphorylated on interaction with organophosphorus inhibitors, plays the main role in it. According to modern ideas[9,10], this chemically inert hydroxyl is activated with the aid of the imidazole group of histidine located in its immediate vicinity. On interaction with the substrate, the activation process begins with formation of a hydrogen bond between its carbonyl oxygen and the imino-nitrogen of imidazole, which increases the basicity of the azole nitrogen and leads to the formation of a hydrogen bond between this nitrogen and the serine hydroxyl[9] (Scheme 1).

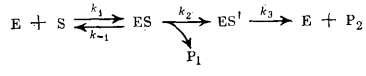
There is then a sharp increase of the nucleophilicity of the hydroxyl oxygen and its interaction with the central carbon atom is facilitated. The redistribution of electron density in the eight-membered ring of the enzyme–substrate complex formed results in the formation of a covalent bond between the serine oxygen and the acid group of the substrate and in the elimination of the alcohol group. The subsequent reaction of the acylated enzyme with water proceeds analogously, forming an intermediate acyl-enzyme–hydrate complex, which then decomposes to the initial enzyme and an acid. Thus the reactive form of the serine hydroxyl is produced at the instant of the oriented binding of the substrate molecule and does not precede it.

The mechanism of cholinesterase hydrolysis presented here is confirmed by a number of facts[4]. Cholinesterases do not catalyse the hydrolysis of choline esters containing thione sulphur (C=S) instead of carbonyl oxygen (C=O), since the sulphur atom is incapable of forming a strong hydrogen bond, which hinders the activation of the serine hydroxyl. For the same reason, organophosphorus compounds containing thione sulphur (P=S) do not phosphorylate cholinesterase, in contrast to their oxygen analogues. Glyceroylcholine, the cyclic structure of the acid group of which has been demonstrated by infrared spectroscopy[11], is not hydrolysed by ACE, because the carbonyl oxygen is already linked by a hydrogen bond to the hydroxy-group of the ester itself:



The hydrolysis of substrates (S) by an enzyme (E) is usually described by Scheme 2[4,12]:

Scheme 2



where ES is the Michaelis complex, ES′ the acylated enzyme, P_1 and P_2 are the alcohol and the acid respectively, and k_1, k_{-1}, k_2, and k_3 are the rate constants for the individual reaction states. Evidently, apart from the complexes ES and ES′, other intermediate complexes, for example, those occurring in Scheme 1, are also formed, but these additional complexes do not, generally speaking, vitiate the kinetic conclusions which follow from the three-stage scheme presented[12].

When the concentration of the substrate [S] in the reaction mixture is many times higher than the initial enzyme concentration $[E]_0$, it is believed that the enzyme hydrolysis proceeds under steady-state conditions where the concentrations of the complexes [ES] and [ES′] are established at almost constant levels. Under these conditions, the scheme leads to the familiar Michaelis–Menten equation

$$v=\frac{a_c[E]_0[S]}{K_M+[S]}=\frac{V[S]}{K_M+[S]}\ , \qquad (1)$$

where v is the rate of hydrolysis of the substrate by the enzyme, V is the maximum velocity of the reaction when the enzyme is fully saturated by the substrate, i.e. for $[S] \gg K_M$, whereupon Eqn.(1) becomes

$$v=V=a_c[E]_0'\ , \qquad (1a)$$

a_C is the activity of the catalytic centre of the enzyme linked to the rate constants of the individual reaction stages by the formula

$$a_c=\frac{k_2k_3}{k_2+k_3} \qquad (1b)$$

and K_M is the Michaelis constant expressed by the formula

$$K_M=\frac{[E][S]}{[ES]+[E']S}=\frac{(k_{-1}+k_2)\,k_3}{k_1(k_2+k_3)}\ . \qquad (1c)$$

When $[S] = K_M$, Eqn.(1) becomes

$$v=\frac{V}{2}\ , \qquad (1d)$$

and it follows from Eqn.(1c) that

$$\frac{K_M}{[S]}=\frac{[E]}{[ES]+[ES']}=1\ , \qquad (1e)$$

where [E] is the concentration of the free enzyme.

Hence it follows that K_M is numerically equal to the substrate concentration for which the rate of the enzyme reaction is smaller by a factor of two than the maximum rate defined by Eqn.(1d) and when half the enzyme is bound in the enzyme–substrate complexes [Eqn.(1e)].

The susceptibility of cholinesterases to irreversible inhibition by organophosphorus inhibitors (OPI) as a result of the phosphorylation of the active centres has been used to determine $[E]_0$ in the enzyme solution investigated[13]; $[E]_0$ is found from the minimum amount of a highly active OPI which fully inhibits the catalytic activity; $[E]_0$ makes it possible to calculate easily the activity of the catalytic enzyme centres a_C from Eqn.(1a): $a_C = V/[E]_0$.

The knowledge of a_C and V for one substrate ($a_{C,1}$ and V_1), for example, for AC, makes it possible to find a_C for another substrate ($a_{C,2}$) from the maximum rate of its enzyme hydrolysis V_2 for the same amount of the preparation of the given enzyme, i.e. for $[E]_{0,1} = [E]_{0,2}$:

$$a_{c,1}/a_{c,2}=V_1/V_2$$

It follows from Eqn.(1a) that a_C characterises the catalytic activity when the enzyme is fully saturated by the substrate, i.e. it does not take into account the first binding stage which has a significant influence on the ability of the enzyme to hydrolyse the substrate at low concentrations. To a first approximation, this stage is assessed in terms of the ratio

$$a_c/K_M : a_c/K_M=k_1k_2/(k_1+k_2)$$

because $k_2/(k_{-1} + k_2) < 1$, so that $a_C/K_M < k_1$.

The ratio a_C/K_M is an important kinetic parameter characterising the catalytic activity of the enzyme in relation to the given substrate when $[S] < K_M$, since under this condition Eqn.(1) becomes

$$v=\frac{a_c[E_0][S]}{K_M}\ . \qquad (1f)$$

Thus at high substrate concentrations the rate of enzyme hydrolysis is determined by the quantity a_C and at low concentrations by the quantity a_C/K_M.

Eqn.(1) is valid for the hydrolysis of the choline esters of carboxylic acids by ACE only at low concentrations of the esters, since at high concentrations the catalytic activity of the enzyme is inhibited. This, the so-called substrate inhibition is taken into account in the Haldane equation[14]

$$v = \frac{V[S]}{K_M + [S] + K_{SS}[S]^2} = \frac{V[S]}{K_M + [S] + (K_M/[S]^2_{opt})[S]^2} \quad (2)$$

where K_{SS} is the substrate inhibition constant.

The quantity K_{SS} is calculated from the formula

$$K_{SS} = K_M/[S]^2_{opt} \quad (2a)$$

where $[S]_{opt}$ is the substrate concentration for which the reaction rate has a maximum, i.e. the substrate concentration corresponding to the maximum on the v–[S] curve[14].

Haldane[14] believes that substrate inhibition is associated with the fact that at high concentrations [S] a second inactive enzyme–substrate sorption complex ES_2 is formed in addition to the ES complexes. At high electrolyte concentrations in the reaction mixture, substrate inhibition of ACE vanishes[15], which is difficult to reconcile with Haldane's hypothesis. Substrate inhibition is probably associated with the interaction of the substrate with an allosteric centre[15].

There is at present no reliable method for determination of the rate constants for the individual stages of the cholinesterase hydrolysis. The study of the kinetics of this reaction is restricted to the determination of K_M and V. One of the commonest procedures for the determination of these kinetic parameters is the Lineweaver–Burk method[16].

Table 1. The cholinesterase hydrolysis of the choline esters of carboxylic acids $RC(O)OCH_2CH_2\overset{+}{N}(CH_3)_3$ (the rate of hydrolysis of AC was assumed to be 100)[4].

Compound	R	BuCE	ACE	Compound	R	BuCE	ACE
(I)	H	180	66	(XI)	$CH_2=CH$	100	12
(II)	CH_3(AX)	100	100	(XII)	$CH_3CH=CH$	20	2
(III)	C_2H_5	180	70	(XIII)	$CH_2=CH-CH_2$	186	11
(IV)	C_3H_7	240	2	(XIV)	$C_2H_5CH=CH$	10	0
(V)	C_4H_9	180	1	(XV)	$CH_2=CHCH_2CH_2$	220	0
(VI)	C_5H_{11}	110	—	(XVI)	$CH_2=C(CH_3)$	47	20
(VII)	C_6H_{13}	120	—	(XVII)	$CH_3CH=C(CH_3)$	11	0
(VIII)	$(CH_3)_2CH$	108	40	(XVIII)	$(CH_3)_2C=CH$	0	0
(IX)	$C_2H_5(CH_3)CH$	13	1	(XIX)	$CH_3CH=C(C_2H_5)$	9	0
(X)	$(C_2H_5)_2CH$	16	0				

II. DIFFERENT ANALOGUES OF ACETYLCHOLINE

The study of the kinetic parameters of the hydrolysis of various carboxylic acid esters by cholinesterases is necessary for the determination of the specificity of their catalytic activity and also for the elucidation of the mechanism of the cholinesterase hydrolysis and of the structure of the active surfaces of these enzymes.

The cholinesterase hydrolysis of AC analogues, differing from the latter either by the structure of the acyl group [$R-C(O)OCH_2CH_2\overset{+}{N}(CH_3)_3$], or the nature of the ester linkage [$R-C(O)XCH_2CH_2\overset{+}{N}(CH_3)_3$], or the structure of the group between the ester oxygen and the onium nitrogen atom [$R-C(O)O-A-\overset{+}{N}(CH_3)_3$], or the structure of the onium group [$CH_3C(O)-OCH_2CH_2\overset{+}{N}R^1R^2R^3$], is discussed below.

1. Substrates Having the General Formula $RC(O)-OCH_2CH_2.\overset{+}{N}(CH_3)_3$

The enzyme hydrolysis of choline esters is known[2–4] to depend significantly on the structure of the acyl residue (Table 1). Among the choline esters of saturated straight-chain carboxylic acids ranging from formic (I) to oenanthic (VII), only the first three esters are hydrolysed by ACE, AC being hydrolysed at the maximum rate, while BuCE hydrolyses all seven esters, the rate of hydrolysis of BuC (IV) being highest.

In contrast to BuC, isobutyrylcholine (VIII), in which the length of the hydrocarbon group in the acyl component is the same as in PrC, is readily hydrolysed by ACE and not less effectively than PrC. It is striking that BuCE hydrolyses isobutyrylcholine less effectively than PrC and BuC, i.e. the branching of the hydrocarbon group impairs the susceptibility of the choline esters to hydrolysis by this enzyme. This is confirmed also by data for the enzyme hydrolysis of the choline esters of ethylmethylacetic (IX) and diethylacetic (X) acids which are hardly hydrolysed by BuCE, while the choline esters of the isomeric straight-chain acids—valeric (V) and caproic (VI)—are hydrolysed by this enzyme at a high rate.

The presence of a double bond in the acyl component reduces the susceptibility of choline esters to cholinesterase hydrolysis. Thus acryloylcholine (XI) is hydrolysed by BuCE and ACE more slowly by factors of almost two and five respectively than its saturated analogue (III). It has been shown in relation to the choline esters of crotonic acid that the influence of the double bond depends greatly on its position. The presence of the double bond in the α-position in compound (XII) reduces sharply the susceptibility of this ester to hydrolysis by BuCE, while the double bond in the β-position in compound (XIII) reduces the rate of hydrolysis of the ester by this enzyme only by a factor of 1.3 compared with BuC. Analogous data have been obtained in experiments with the choline esters of unsaturated analogues of valeric acid [compounds (XIV) and (XV)][4].

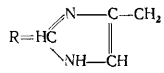
Unusual results have been obtained for the choline esters of aminoacids in which $R = NH_2(CH_2)_n$.[17] Under the influence of BuCE, the rates of hydrolysis of esters with $n = 3–4$ were lower by a factor of 15–20 than the rate of hydrolysis of AC and for $n = 6$ and 7 these esters were hydrolysed at the same rate as AC. The conversion of NH_2 into $\overset{+}{N}(CH_3)_3$ leads in all cases to a sharp reduction of the rate of enzyme hydrolysis[17].

It has been shown[18] that carbamoylcholine ($R = NH_2$) is not hydrolysed at all by BuCE.

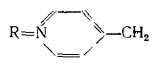
Interesting data have been obtained[19,20] for the cholinesterase hydrolysis of fluoro-, chloro-, bromo-, and iodo-substituted AC derivatives. All these derivatives were hydrolysed faster by BuCE than AC (by a factor greater than 2.5), the bromo-derivative being hydrolysed at the maximum rate. The inhibition of catalytic activity by high substrate concentrations, which is atypical for BuCE, was observed for all the derivatives. The fluoro-derivative was hydrolysed by ACE like AC, while the remaining derivatives were hydrolysed more slowly by a factor of two, despite the fact that in all of them the strength of the ester linkage is much lower than in AC. Obviously the observed effect of the substitution of a hydrogen atom by a halogen is associated with the increase of the size of the acid group. This hypothesis is confirmed by the fact that the dichloro-derivative of AC is hydrolysed by ACE five times more slowly than AC, while the trichloro-derivative is not hydrolysed at all. It is surprising that BuCE, for which the steric factor should not play a

significant role in the given instance, does not hydrolyse these two esters.

The introduction into the acyl part of the AC molecule of the imidazole group[21]

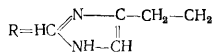


and the pyridine group[22]



reduced the rate of hydrolysis by BuCE, while ACE altogether failed to hydrolyse these derivatives.

It is striking that imidazolylpropionylcholine



is hydrolysed by BuCE as effectively as BuC, i.e. 2.5 times faster than AC[21].

At high concentrations phenylpropionylcholine ($R=C_6H_5CH_2.CH_2$) is hydrolysed by BuCE almost twice as fast as AC and BzC, while at low concentrations it is hydrolysed faster by a factor greater than 40 owing to the lower value of K_M; it is not hydrolysed by ACE[23]. As for the imidazole derivatives, an increase of the distance between the carbonyl carbon and the phenyl group leads to an appreciable increase of the rate of enzyme hydrolysis.

The stereospecificity of cholinesterases has been investigated in experiments with lactoylcholine. The L(+)- isomer was hydrolysed by ACE faster than AC by a factor of 1.5, while the rate of hydrolysis of the D(-)-isomer was five times lower; the rate of hydrolysis of the racemate was 70% of that of AC[11]; BuCE did not exhibit stereospecificity: both isomers were hydrolysed by this enzyme 3.5 times faster than AC[24].

Thus the data examined in this section show that ACE is more sensitive than BuCE to changes in the structure of the acid components of the molecules of choline esters.

2. Substrates Having the General Formula $RC(O)XC_2H_4\overset{+}{N}(CH_3)_3$

Analogues of AC are known in which the ester oxygen has been replaced by S, Se, and NH. Among them, the greatest interest attaches to the thiocholine esters, whose study was begun as early as 1939[18]. Acetylthiocholine (ATC) and butyrylthiocholine (BuTC) have already been used for a long time in histological investigations in order to discover and locate cholinesterases in various tissues. These esters as well as propionylthiocholine (PrTC) and acetyl-β-methylthiocholine (AMTC) are also widely used in biochemistry in the study of the catalytic activities of cholinesterases; the thiocholine formed on their hydrolysis can be readily determined colorimetrically with the aid of the Ellman chromogen reagent[25]. This method for the determination of the cholinesterase activity is more sensitive than the potentiometric method.

Data according to which the rate of hydrolysis of thiocholine esters by cholinesterases is several times higher than that of the choline analogues have been presented in a series of reviews and monographs[2,3,5,6]. It has been demonstrated convincingly[26,27] that the available literature data are much too high, since the investigators who used the potentiometric titration method did not take into account the acid properties of the thiocholine formed on hydrolysis of these substrates.

Table 2 presents the results of a comparative kinetic study of the enzyme hydrolysis of choline and thiocholine esters by ACE and BuCE[27].

All the relations established for the oxygen analogues are valid for the cholinesterase hydrolysis of the thiocholine esters. Thus ATC is hydrolysed fastest by ACE, PrTC is hydrolysed more slowly, and BuTC is hardly hydrolysed at all. The rate of hydrolysis by BuCE decreases in the sequence BuTC > PrTC > ATC. The inhibition of enzyme activity by high concentrations of thiocholine esters is manifested only in experiments with ACE. There are also similarities between other substrate properties of thiocholine and choline esters—an S optimum and a pH optimum. It is striking that at high substrate concentrations ACE hydrolyses AC at a higher rate (in terms of a_C), while at low concentrations the rate of hydrolysis of ATC is higher (in terms of a_C/K_M). Butyrylcholinesterase hydrolyses ATC faster than AC at both high and low concentrations.

In contrast to its oxygen analogue, AMTC is hydrolysed comparatively effectively by BuCE and cannot therefore be used as a specific substrate of ACE[26,28].

Table 2. Kinetic parameters of the hydrolysis of choline and thiocholine esters by BuCE and ACE[27].

Substrate	BuCE			ACE		
	a_c, min^{-1}	K_M, mol $litre^{-1}$	a_c/K_M, litre mol^{-1} min^{-1}	a_c, min^{-1}	K_M, mol $litre^{-1}$	a_c/K_M, litre mol^{-1} min^{-1}
AC	$7.6\cdot10^4$	$9.1\cdot10^{-4}$	$8.4\cdot10^7$	$2.8\cdot10^5$	$1.9\cdot10^{-4}$	$1.5\cdot10^9$
PrC	$1.2\cdot10^5$	$5.5\cdot10^{-4}$	$2.2\cdot10^8$	$2.2\cdot10^5$	$2.8\cdot10^{-4}$	$8.0\cdot10^8$
BuC	$2.1\cdot10^5$	$7.7\cdot10^{-4}$	$2.7\cdot10^8$	0	—	—
ATC	$9.5\cdot10^4$	$5.4\cdot10^{-4}$	$1.8\cdot10^8$	$2.2\cdot10^5$	$1.0\cdot10^{-4}$	$2.2\cdot10^9$
PrTC	$1.2\cdot10^5$	$5.1\cdot10^{-4}$	$2.4\cdot10^8$	$1.2\cdot10^5$	$1.9\cdot10^{-4}$	$6.0\cdot10^8$
BuTC	$1.6\cdot10^5$	$4.3\cdot10^{-4}$	$3.8\cdot10^8$	0	—	—

The observed differences between the abilities of ACE and BuCE to hydrolyse choline and thiocholine esters are due to different causes: the different amounts of anhydride character in the ester linkages, the different configurations of the choline and thiocholine esters, and the different radii of the heteroatoms.

The selenium analogue of AC was hydrolysed by ACE at a lower rate than ATC[29]. It was believed that the amide analogue of AC (X = NH) cannot be hydrolysed by cholinesterases[4]. However, according to the latest data[30], this substrate is hydrolysed by ACE. In the study of the rate of hydrolysis of this amide one must bear in mind that the trimethylaminoethylammonium cation $(CH_3)_3\overset{+}{N}CH_2CH_2NH_2$ has pronounced basic properties and the traditional potentiometric titration method is not suitable for its determination.

3. Substrates Having the General Formula $RC(O)OAN(CH_3)_3$

The susceptibility of choline esters to hydrolysis by cholinesterases is greatly influenced by the structure of the group A between the ester oxygen and the onium nitrogen atom. Several AC derivatives in which the hydrogen atoms in the ethylene chain have been substituted by various hydrocarbon groups ($A = -CHR^1CHR^2$) have been synthesised. The β-methyl derivative of AC, which is relatively easily hydrolysed by ACE, is of greatest interest: the rate of its hydrolysis is smaller by a factor of three than that of AC[31] and it is hardly hydrolysed by BuCE (at least 20 times more slowly than AC[32]). Until recently, acetyl-β-methylcholine was therefore regarded as the only specific substrate

of ACE. The substitution of the hydrogen in the β-position by more complex hydrocarbon groups ranging from C_2H_5 to C_6H_{13} increases only slightly the rate of hydrolysis of esters by BuCE[18]. Unfortunately the hydrolysis of these AC derivatives by ACE has not been investigated.

The specificity of ACE to the acyl residue of the β-methylcholine esters is the same as for choline esters: the propionate hydrolyses more slowly than the acetate, the rate of hydrolysis of the isobutyrate is lower still, and trimethylacetate is not hydrolysed at all[33].

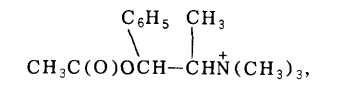
Experiments with the optical isomers of acetyl-β-methylcholine established that the L-isomer is hydrolysed by ACE more slowly by a factor of two than AC, while the D-isomer proved to be a reversible inhibitor and not a substrate. As mentioned above, the racemate is hydrolysed by this enzyme approximately three times more slowly than AC.

In experiments with butyryl-β-methylcholine it was shown that stereospecificity is characteristic also of BuCE: the L-isomer is hydrolysed by this enzyme 10 times more slowly than AC, while the D-isomer is not hydrolysed at all. It is striking that the stereospecificity of both enzymes is not shown in the hydrolysis of acetyl-β-methylcholine: both isomers are hydrolysed by BuCE more slowly by a factor of 1.5 than AC[34], while the rate of hydrolysis by ACE is the same as that of AC[33].

Thus the stereospecificity of cholinesterases is not manifested in all hydrolytic reactions of optically active substrates: it depends significantly on the position of the asymmetric carbon atom in the substrate molecule. The stereospecificity depends also on the nature of the enzyme. As stated above, ACE can distinguish between the D- and L-isomers of lactoylcholine, while BuCE cannot.

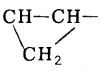
The replacement of two hydrogen atoms in the ethylene group by a methyl group in the α- and β-positions lowers the rate of hydrolysis of this ester by ACE[35]. Since there are two asymmetric carbon atoms in the acetyl-α,β-dimethylcholine molecule, this ester should exist in the form of four isomers, forming two pairs: the *erythro*-isomers and the *threo*-isomers, each pair constituting optical enantiomers. It was found that ACE hydrolyses only the *threo*-α(R), β(S)-dimethyl-AC racemate, while the rate of hydrolysis of *erythro*-α(R), β(S)-dimethyl-AC is zero[55].

The esters having the general formula



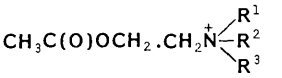
$$CH_3C(O)OCH(C_6H_5)-CH(CH_3)\overset{+}{N}(CH_3)_3,$$

which are synthesised from ephedrine and pseudoephedrine and are the α-methyl and β-phenyl derivatives of AC, are not hydrolysed by cholinesterases and behave as reversible inhibitors[36].

When the ethylene group in the AC molecule was replaced by the "rigid" cyclopropyl group (A = ), the optically active *trans*- and *cis*-isomers were obtained[37]. The rates of hydrolysis of the (+)- and (-)-*trans*-isomers by ACE were 96% and 59% of that of AC respectively. They were hydrolysed at a lower rate by BuCE: 61 and 33% respectively. The *cis*-isomers were not hydrolysed by these enzymes.

The data described here lead to the conclusion that BuCE is more sensitive to changes in the structure of the ethylene group in the AC molecule than ACE. This conclusion is also confirmed by the results of experiments with AC analogues in which the ethylene group has been replaced by a longer alkyl chain: $A = -(CH_2)_n-$. The ester with the trimethylene chain is hydrolysed by the rat brain homogenate ACE at 70% of the rate of hydrolysis of AC, while the ester with the tetramethylene chain is hydrolysed at 10% of the AC rate. On the other hand, under the influence of BuCE, the rates of their hydrolysis are 7.2 and 0.6% respectively[18,38,39]. Analogous data indicating a decrease of the catalytic activity of cholinesterases with increase of *n* have been obtained in experiments with ammonium and sulphonium compounds[40,41]. The high sensitivity of BuCE to an increase in the length of the alkyl chain has also been demonstrated in experiments with analogous BuC derivatives. The esters with the trimethylene and tetramethylene chains are hydrolysed by this enzyme respectively 5 and 70 times more slowly than BuC[42].

4. Substrates Having the General Formula



$$CH_3C(O)OCH_2.CH_2\overset{+}{N}(R^1)(R^2)(R^3)$$

The susceptibility of various analogues of AC to hydrolysis by cholinesterases depends also on the structure of the ammonium group. Thus the replacement of three methyl groups at the onium nitrogen in AC by ethyl groups resulted in a sharp decrease of the rate of their hydrolysis by BuCE but hardly affected the rate of hydrolysis by ACE[43].

It follows from the data in Table 3[44] that, among the compounds investigated, only the dibutylmethyl derivative (XXIX) proved to be an inhibitor and not a substrate of cholinesterases. Evidently such a large increase in the bulk of the ammonium group should result in a loss by AC derivatives of susceptibility to cholinesterase hydrolysis. Other AC derivatives, except compound (XXI), were hydrolysed by cholinesterases at high concentrations in the reaction mixture but at a lower rate than AC: this is indicated by the values of a_C listed in Table 3. According to the literature[43], a change in the composition of the ammonium group entails a more marked alteration of a_C in experiments with BuCE. Apparently the presence of a charge is most important for ACE, while a change in the structure of the ammonium group is less significant than for BuCE.

When the methyl groups in the AC molecule are replaced by ethyl groups, as in compound (XXVII), the parameter a_C decreases by a factor of 3 for BuCE and only by 1/3 for ACE. Analogous ratios were obtained also for other derivatives, except the pentyl derivative (XXIV), for which a_C in experiments with ACE fell by a factor of two compared with a_C for AC, while in experiments with BuCE the decrease was only by 1/4. It is of interest that the isopropyl derivative (XXV) is very similar to its unbranched analogue (XXII) as a substrate of BuCE and ACE.

The values of K_M for many compounds, with the exception of (XXI), (XXIV), (XXV), and (XXVII) in experiments with ACE and (XXVIII) in experiments with BuCE, proved to be lower than for ACE.

The observed differences between the values of a_C for cholinesterases in the enzyme hydrolysis of AC analogues as a function of the composition of the ammonium group conflict with Scheme 2 and Eqn.(1) which follows from it. Since all these compounds are acetate esters, the deacetylation rate constants k_3 for their ES′ complexes should be the same. The acetylation rate constants k_2 should also be virtually the same, since, according to quantum-chemical calculations, all the compounds are characterised by the same electron density at the carbonyl carbon atom and the strengths of the ester linkages should not therefore differ either. Thus, in conformity with this finding, when Scheme 2 is valid for all the compounds quoted, the values of a_C should also be identical in experiments with both ACE and BuCE. In fact these quantities vary within wide limits.

Table 3. Kinetic parameters of the hydrolysis of AC analogues having the general formula $CH_3C(O).OC_2H_4X$ by BuCE and ACE[44].

Compound	X	BuCE						ACE					
		a_c, min^{-1}	K_M, M mol $litre^{-1}$	a_c/K_M, litre mol^{-1} min^{-1}	p	K_M^*, M mol $litre^{-1}$	K_b, M mol $litre^{-1}$	a_c, min^{-1}	K_M, M mol $litre^{-1}$	a_c/K_M, litre mol^{-1} min^{-1}	p	K_M^*, M mol $litre^{-1}$	K_b, M mol $litre^{-1}$
(XX)	$\overset{+}{N}(CH_3)_3$ (AX)	$6.0\cdot10^4$	$5.0\cdot10^{-4}$	$1.2\cdot10^8$	1	$5\cdot10^{-4}$	—	$3.0\cdot10^5$	$2\cdot10^{-4}$	$15\cdot10^8$	1	$2.0\cdot10^{-4}$	—
(XXI)	$\overset{+}{N}(CH_3)_2C_2H_5$	$6.0\cdot10^4$	$3.3\cdot10^{-4}$	$1.8\cdot10^8$	1	$3.3\cdot10^{-4}$	—	$3.1\cdot10^5$	$2\cdot10^{-4}$	$15\cdot10^8$	1	$2\cdot10^{-4}$	—
(XXII)	$\overset{+}{N}(CH_3)_2C_3H_7$	$1.9\cdot10^4$	$3.7\cdot10^{-4}$	$0.5\cdot10^8$	0.12	$12\cdot10^{-4}$	$5.4\cdot10^{-4}$	$2.2\cdot10^5$	$1.8\cdot11^{-4}$	$12\cdot10^8$	0.73	$2.5\cdot10^{-4}$	$6.7\cdot10^{-4}$
(XXIII)	$\overset{+}{N}(CH_3)_2C_4H_9$	$2.2\cdot10^4$	$2.3\cdot10^{-4}$	$1.0\cdot19^8$	0.37	$6.2\cdot10^{-4}$	$3.7\cdot10^{-4}$	$1.6\cdot10^5$	$3.8\cdot10^{-4}$	$4\cdot10^8$	0.54	$6.9\cdot10^{-4}$	$8\cdot10^{-4}$
(XXIV)	$\overset{+}{N}(CH_3)_2C_5H_{11}$	$4.8\cdot10^4$	$2.8\cdot10^{-4}$	$1.7\cdot10^8$	0.8	$3.5\cdot10^{-4}$	$14\cdot10^{-4}$	$1.6\cdot10^5$	$1.4\cdot10^{-4}$	$11\cdot10^8$	0.54	$2.6\cdot10^{-4}$	$3.1\cdot10^{-4}$
(XXV)	$\overset{+}{N}(CH_3)_2CH(CH_3)_2$	$1.9\cdot10^4$	$4.1\cdot10^{-4}$	$0.5\cdot10^8$	0.32	$13\cdot10^{-4}$	$6\cdot10^{-4}$	$2.5\cdot10^5$	$1.6\cdot10^{-4}$	$16\cdot10^8$	0 85	$1.9\cdot10^{-4}$	$10\cdot10^{-4}$
(XXVI)	$\overset{+}{N}(C_2H_5)_2CH_3$	$4.5\cdot10^4$	$4.4\cdot10^{-4}$	$1.0\cdot10^8$	0.75	$5.9\cdot10^{-4}$	$18\cdot10^{-4}$	$2.6\cdot10^5$	$1.7\cdot10^{-4}$	$15\cdot10^8$	0.87	$2.0\cdot10^{-4}$	$13\cdot1^{-4}$
(XXVII)	$\overset{+}{N}(C_2H_5)_3$	$2.1\cdot10^4$	$2.9\cdot10^{-4}$	$0.7\cdot10^8$	0.35	$8.3\cdot10^{-4}$	$4,5\cdot10^{-4}$	$1,9\cdot10^5$	$2.6\cdot10^{-4}$	$7\cdot10^8$	0,64	$4.1\cdot10^{-4}$	$7.2\cdot10^{-4}$
(XXVIII)	$\overset{+}{N}(C_3H_7)_2CH_3$	$0.3\cdot10^4$	$12\cdot10^{-4}$	$0.02\cdot10^8$	0.05	$240\cdot10^{-4}$	$13\cdot10^{-4}$	$0.32\cdot10^5$	$9\cdot10^{-4}$	$0.4\cdot10^8$	0.11	$82\cdot10^{-4}$	$10\cdot10^{-4}$
(XXIX)	$\overset{+}{N}(C_4H_9)_2CH_3$	0	$1\cdot10^{-3}$ [a]	—	0	—	—	—	$1\cdot10^{-4}$ [a]	—	0	—	—

Note. K_M^* is the true Michaelis constant, K_b the equilibrium dissociation constant of the inactivated complex, and p a coefficient defining the fraction of productive binding of the substrate in enzyme hydrolysis.

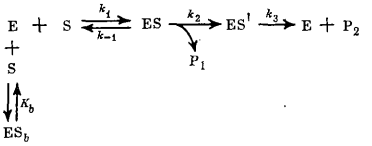
[a] The reversible inhibition constant K_i is quoted.

The resulting contradiction can be readily resolved on the hypothesis of productive and non-productive binding[45-47]. According to this hypothesis, enzyme hydrolysis can occur only for the correct orientation of the substrate molecule on the active surface of the enzyme, i.e. under the conditions of productive binding where the carbonyl carbon atom of the substrate occupies a rigorously defined position relative to the serine hydroxyl, which attacks this carbon atom.

Evidently the probability of the correct orientation is not sufficiently high for all the AC analogues. If, following the binding of the substrate, its carbonyl carbon atom is not in the immediate vicinity of the serine hydroxyl, hydrolysis cannot occur. Such binding with an incorrect orientation is referred to as non-productive binding.

Taking into account non-productive binding, the scheme for cholinesterase hydrolysis becomes:

Scheme 3



where K_b is the equilibrium dissociation constant of the inactive complex ES_b. Scheme 3 leads to a modification of the Michaelis–Menten equation:

$$v=\frac{a_c[E]_0[S]}{K_M+[S]}=\frac{(k_2+k_3)/(k_2\cdot k_3)\cdot K_b/(K_b+K_M^*)[E]_0[S]}{(K_M^*K_b/(K_b+K_M^*))+[S]}=\frac{a_c^*p[E]_0[S]}{K_M^*p+[S]}\quad\ldots,\quad(5)$$

where K_M and a_c are the Michaelis constant and the activity of the catalytic centre, which are determined experimentally, K_M^* and a_c^* are the true values of these parameters expressed by Eqns.(1c) and (1b), and p is a coefficient which defines the fraction of the productive binding of the substrate in the enzyme hydrolysis:

$$p=\frac{[ES]+[ES']}{[ES]+[ES']+[ES_b]}=\frac{K_b}{K_b+K_M^*}\quad.\qquad(6)$$

If $K_b > K_M^*$, then $[ES_b] \to 0$ and $p = 1$, so that $a_c = a_c^*$ and $K_M = K_M^*$. In this case there is no non-productive binding and each substrate molecule sorbed on the active centre hydrolyses. On the other hand, if $K_b < K_M$, non-productive binding mainly takes place: $p = K_b/K_M^* \to 0$, $a_c = a_c p \to 0$, and under these conditions the ester is a reversible inhibitor and not a substrate. Probably at equal enzyme concentrations $[E]_0$ the differences between the experimental values of $a_c = a_c p$ [see Eqn.(5)] for the AC analogues are related mainly to the different values of the coefficient p; on the other hand, the true catalytic activities a_c for these substances should be the same for the reasons indicated above. In this case the ratio of the values of a_c for two substrates should be equal to the ratio of the coefficients p:

$$a_{c;1}/a_{c;2}=a_{c;1}^*p_1/a_{c;2}^*\cdot p_2=p_1/p_2\quad.\qquad(7)$$

The value of p for each AC analogue with a modified composition of the ammonium group can be estimated assuming that $p = 1$ in the enzyme hydrolysis of AC neglecting thereby the non-productive binding of AC on both ACE and BuCE:

$$p=a_c/a_c(AX)\quad.\qquad(8)$$

The values of p found for the acetates investigated make it possible to calculate for them the K_b and the true Michaelis constants K_M^*:

$$K_M^*=K/p\quad,\qquad(9)$$

$$K_b=K_M^*p/(1-p)\quad.\qquad(10)$$

The ratio a_c/K is of fundamental importance for the kinetics of enzymic reactions. Firstly, it does not depend on the non-productive sorption and, when account is taken of Eqns.(8), (9), and (10), we have

$$a_c/K_M=a_c^*\cdot p/K_M^*p=a_c^*/K_M^*=\frac{k_2k_3k_1(k_2+k_3)}{(k_2+k_3)(k_{-1}+k_2)k_3}=k_1\frac{k_2}{k_{-1}+k_2}\quad.\qquad(11)$$

Secondly, this ratio makes it possible to estimate the rate constant for the formation of the Michaelis complex—since $k_2/(k_{-1} + k_2) < 1$, it follows from Eqn.(11) that $k_1 > a_c/K$.

Thirdly, the ratio a_c/K_M characterises the rate of reaction for $[S] \ll K_M$, whereupon Eqn.(1) becomes

$$v = \frac{a_c}{K_M} \cdot [E]_0 [S] .$$

Calculations have shown that the markedly lower a_c for the butyrylcholinesterase hydrolysis of the AC analogues investigated compared with the acetylcholinesterase hydrolysis is associated with a more significant alteration of p. If compound (XXII) is excluded, then a_c is reduced by a factor less than two in experiments with ACE for all other AC analogues, while in experiments with BuCE the reduction is by a factor of three. When account was taken of non-productive binding, the true Michaelis constants K_M^* increased appreciably. In most cases they are inversely proportional to the ratios a_c/K_M, which, as stated above, characterise to a first approximation the rate constant for the productive binding of the substrate to the enzyme (k_1). Indeed substrates with the highest K_M^* are characterised by the lowest ratios a_c/K: (XII) and (XXV) in experiments with BuCE and (XXIII) and (XXVII) in experiments with ACE. The observed correlation between K_M^* and a_c/K_M shows that the changes in the true Michaelis constants K_M^* for the AC analogues investigated are associated mainly with the changes in k_1, while the rate constants for other steps in enzyme hydrolysis, namely k_2 and k_3, and possibly also k_{-1}, do not vary[45-47].

Compound (XXVIII), which can be logically regarded as an inhibitor, is not an exception. It is characterised by the highest K_M^* and the lowest ratio a_c/K_M in view of the extremely small contribution of productive sorption. On the basis of the idea of productive and non-productive binding, the calculated K_b should be smallest for substrates with the smallest p. Such a relation has been traced in relation to many AC analogues in experiment with BuCE: compounds (XXIV) and (XXVI) have the highest values of p and the highest K_b, while compounds (XXII), (XXIII), and (XXVII) have the lowest p and K_b. In experiments with ACE this relation is less clear-cut. The observed scatter of the calculated data is associated, firstly, with the assumption that $p = 1$ for AC and, secondly, with the inevitable errors in the experimental determination of V and K_M, particularly for ACE, whose catalytic activity is suppressed by high substrate concentrations. The question arises of the cause responsible for the alteration of the contribution of productive binding for the AC analogues investigated. In the cholinesterase hydrolysis of choline esters, the sorption of the latter is ensured in the first place by the ion–ion interaction of the ammonium group of the substrate with the anionic site of the CE. Furthermore, the hydrophobic interaction of the hydrocarbon groups of the "cationic head" of the substrate with the hydrophobic region surrounding the anionic centre plays a significant role.

The complementarity of the substrate molecule in relation to the active surface of the enzyme, which is ultimately responsible for productive sorption, depends in general on the extent to which the ion–ion, ion–dipole, and hydrophobic interactions are concerted. When the interactions are concerted, the substrate molecule occupies a position on the active centre such that the necessary conditions are created for the formation of a reactive Michaelis complex (see Scheme 1). In such productive binding of the substrate, the activation of the serine hydroxyl, which executes a nucleophilic attack on the carbonyl carbon atom, is ensured.

When the above interactions of the substrate molecule with the active surface of the enzyme are not concerted, conditions, for the formation of the Michaelis complex are not created. An enzyme–substrate complex ES_b, inert with respect to the reaction, is formed instead.

In the light of this hypothesis, the enhancement of the hydrophobic interaction as a result of the introduction of more complex hydrocarbon groups into the substrate molecule should not always result in an increased contribution of the productive binding of the substrate to the enzyme. For example, in experiments with BuCE the parameter a_c decreases respectively by a factor greater than two, 2.7, and only 1.3 when the methyl group in the AC molecule is replaced by a propyl group [compound (XXIV)], by a butyl group [compound (XXV)], and by a pentyl group [compound (XXVI)].

Theoretical conformational analysis showed that such an unusual alteration of a_c on gradual substitution of one methyl group at the onium nitrogen atom by more complex groups is associated with the alteration of the steric configuration of the substrate molecules occurring under these conditions. It has been shown that even a slight change in the ammonium group alters the number of stable conformations, among which only some are compatible with the active surface of the enzyme. Hence the change in the contribution of the non-productive sorption of the substrate is associated with the change in the quantitative ratio of the conformers, both complementary and non-complementary, in relation to the active surface of the enzyme[48].

III. ESTERS WITH A CYCLIC AMMONIUM GROUP IN THE ALCOHOL COMPONENT OF THE MOLECULE

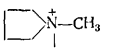
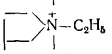
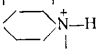
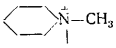
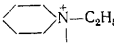
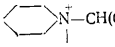
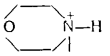
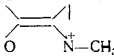
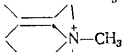
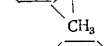
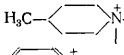
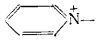
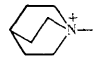
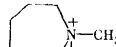
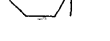
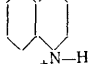
Since 1939[18] numerous esters of this kind have been investigated. Among them, extremely valuable cholinesterase substrates have been discovered. This applies in the first place to the chomogen and fluorogen substrates, which differ significantly in their optical properties from their hydrolysis products[49]. The use of these substrates makes it possible to determine the activities of cholinesterases with a high accuracy even at very low enzyme and substrate concentrations.

This section deals with two types of acetates of cyclic aminoalcohols: esters in which the acetoxyethyl group is linked to an onium nitrogen [$CH_3C(O)OCH_2CH_2\overset{+}{N}$] and esters in which the acetoxy-group is linked to rings containing an onium nitrogen atom. In addition, certain thio-derivatives are also considered.

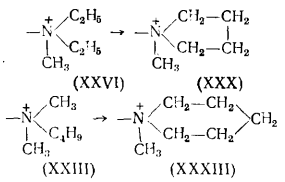
1. Esters Having the General Formula $CH_3C(O)OCH_2CH_2\overset{+}{N}$

These esters can be regarded as AC analogues. Their study was begun comparatively recently[47]. The compounds listed in Table 4 have been synthesised and the kinetics of their cholinesterase hydrolysis have been investigated by large teams of chemists and biochemists at the Institute of Bio-organic Chemistry of the Academy of Sciences of the Uzbek SSR, the Institute of Experimental Medicine of the Academy of Medical Sciences of the USSR, and the Sechenov Institute of Evolutionary Physiology and Biochemistry of the USSR Academy of Sciences[4,36,44,47,50-64]. Compounds (XXX)–(XXXIII) are of special interest, because the effect of the cyclisation of the ammonium group can be demonstrated in

Table 4. Kinetic parameters of the reactions of the cyclic aminoalcohol acetates $CH_3C(O)OC_2H_4X$ with BuCE and ACE.

Compound	X	BuCE			ACE		
		a_c, min^{-1}	K_M, mol $litre^{-1}$	a_c/K_M, litre $mol^{-1}min^{-1}$	a_c, min^{-1}	K_M, mol $litre^{-1}$	a_c/K_M, litre $mol^{-1}min^{-1}$
(XXX)		$1.3\cdot10^4$	$1.7\cdot10^{-4}$	$7.7\cdot10^7$	$2.5\cdot10^5$	$2.6\cdot10^{-4}$	$1.0\cdot10^9$
(XXXI)		$3.2\cdot10^4$	$2.5\cdot10^{-4}$	$1.3\cdot10^8$	$2.5\cdot10^5$	$1.8\cdot10^{-4}$	$1.4\cdot10^9$
(XXXII)		0	—	—	0	—	—
(XXXIII)		$3.0\cdot10^3$	$4.0\cdot10^{-5}$	$7.5\cdot10^7$	$1.9\cdot10^5$	$5.0\cdot10^{-4}$	$3.8\cdot10^8$
(XXXIV)		$2.0\cdot10^4$	$1.8\cdot10^{-4}$	$1.1\cdot10^8$	$1.6\cdot10^5$	$5.0\cdot10^{-4}$	$8.0\cdot10^8$
(XXXV)		$3.9\cdot10^4$	$3.3\cdot10^{-4}$	$1.2\cdot10^8$	$9.0\cdot10^4$	$3.3\cdot10^{-4}$	$2.7\cdot10^8$
(XXXVI)		0	—	—	0	—	—
(XXXVII)		$4.1\cdot10^3$	$8.0\cdot10^{-4}$	$5.1\cdot10^6$	$1.4\cdot10^5$	$6.7\cdot10^{-4}$	$2.1\cdot10^8$
(XXXVIII)		$3.1\cdot10^3$	$3.4\cdot10^{-4}$	$9.0\cdot10^6$	$1.1\cdot10^5$	$7.0\cdot10^{-4}$	$1.6\cdot10^8$
(XXXIX)		$1.2\cdot10^4$	$1.8\cdot10^{-4}$	$6.7\cdot10^7$	$1.9\cdot10^5$	$1.5\cdot10^{-3}$	$1.3\cdot10^8$
(XL)		0	—	—	0	—	—
(XLI)		0	—	—	0	—	—
(XLII)		$4.0\cdot10^3$	$8.0\cdot10^{-4}$	$5.0\cdot10^6$	$1.4\cdot10^5$	$6.7\cdot10^{-4}$	$2.1\cdot10^8$
(XLIII)		0	—	—	0	—	—
(XLIV)		$1.6\cdot10^3$	$2.1\cdot10^{-4}$	$7.5\cdot10^6$	$3.2\cdot10^4$	$1.2\cdot10^{-4}$	$2.6\cdot10^8$
(XLV)		$1.8\cdot10^3$	$2.8\cdot10^{-5}$	$6.5\cdot10^7$	$1.7\cdot10^4$	$3.0\cdot10^{-5}$	$5.6\cdot10^8$
(XLVI)		$1.7\cdot10^3$	$2.2\cdot10^{-5}$	$7.2\cdot10^7$	$1.5\cdot10^4$	$3.1\cdot10^{-5}$	$4.9\cdot10^8$
(XLVII)		$6.0\cdot10^2$	$1.2\cdot10^{-4}$	$5.0\cdot10^6$	$7.4\cdot10^3$	$1.2\cdot10^{-4}$	$6.0\cdot10^7$
(XLVIII)		0	—	—	0	—	—

relation to them:



(XXVI) (XXX)

(XXIII) (XXXIII)

These processes are accompanied by a sharp decrease of a_C for BuCE but hardly affect the reactions with ACE. The expansion from the five-membered ring in compound (XXX) to the seven-membered ring in compound (XLII) is accompanied by a gradual decrease of a_C by a factor of 3–4 for BuCE and less than two for ACE. The data presented demonstrate as a whole a greater sensitivity of BuCE to changes in the structure of the ammonium group. This conclusion is consistent with that based on the study of the substrates (XX)–(XXIX) in Table 3.

The introduction of a methyl group in the α-position of the piperidine ring [compound (XXXVIII)] reduces a_C for ACE, while the introduction of a methyl group in the γ-position [compound (XXXIX)] increases a_C for BuCE. On the other hand, the derivative with a pyridinium group in the α-position [the anabasine derivative (XLVIII)] is not hydrolysed by these enzymes. The replacement of the pyridinium group by the piperidinium group [compound (XL)] or by the rigid quinuclidinium group (XLI) results in a complete loss of susceptibility to hydrolysis by cholinesterases.

The increase in the bulk of the cyclic ammonium group [compounds (XLIV), (XLV), (XLVI), and (XLVII)] is accompanied by an appreciable decrease of a_C for ACE and BuCE. There is little difference between the substrate properties of the piperidinium compound and the more hydrophilic morpholinium compound (XXXVII). The *N*-ethyl derivatives (XXXI) and (XXXIV) are hydrolysed by BuCE much more effectively than their *N*-methyl analogues.

The constants K_M for the substrates investigated vary: by a factor of 35 for BuCE [compounds (XLII) and (XLVI)] and by a factor of 50 for ACE [compounds (XXXIX) and (XLV)]. As pointed out above, the constants K_M do not by themselves characterise the susceptibility of substrates to hydrolysis by cholinesterases. They are important in estimates of this susceptibility at low substrate concentrations, where the rate of hydrolysis is determined by the quantity a_C/K_M. It is striking that compound (XLVII), with the smallest values of a_C for these enzymes, has also the smallest value of a_C/K_M and that the maximum value of a_C/K_M corresponds to the maximum value of a_C: compound (XXXI) for ACE and compound (XXXV) for BuCE.

The fact that the tertiary analogues of the cyclic esters (XXXII), (XXXVI), and (XLIII) are not hydrolysed by ACE and BuCE is of special interest. Here it is appropriate to recall that dimethylaminoethyl acetate, a tertiary analogue of AC, is hydrolysed 1.5–3 times more slowly by BuCE and ACE than AC. According to the results of theoretical conformational analysis[65], the cyclic conformation of dimethylaminoethyl acetate with the C=O...H–N hydrogen bond is the most favourable. As stated above, the formation of a hydrogen bond between the carbonyl oxygen of AC and the imidazole ring of histidine in the active centre of the enzyme plays an important role in cholinesterase catalysis and such cyclic conformers are not therefore hydrolysed although their sorption on the catalytic surface is not ruled out.

As regards the lack of susceptibility of the cyclic aminoalcohol tertiary esters (XXXII), (XXXVI), and (XLII) to cholinesterase hydrolysis, conformational calculations have shown that the structure of the acetoxyethyl component in the equatorial position relative to the nitrogen-containing ring is energetically favourable. This less compact conformation, compared with the axial conformation, should suffer from steric hindrance by the hydrophobic groups surrounding the anionic centre of the enzyme, which is an additional cause whereby one can explain their lack of susceptibility to hydrolysis by cholinesterases.

2. Esters Having the General Formula $RC(O)S(CH_2)_2R$

It follows from Table 2 that the replacement of the ester oxygen by sulphur in the choline substrate molecules does not entail a significant change in their susceptibility to cholinesterase hydrolysis. Large changes in such susceptibility are observed when O is replaced by S in acetyl-β-methylcholine (AMC). Whereas AMC itself is hydrolysed by BuCE at a very low rate ($a_C = 3 \times 10^3$ min^{-1}), its thiol analogue (AMTC) is hydrolysed by this enzyme 20 times faster ($a_C = 6.5 \times 10^4$ min^{-1}).[28] The parameter a_C for ACE increases only by a factor of two (1.0×10^5 and 2.1×10^5 min^{-1} respectively)[28]. The replacement of O by S in the AMC molecule therefore results in a sharp decrease of specificity: the ratios a_C(ACE)/a_C(BuCE) for AMC and AMTC are respectively 30 and 3.

It was therefore of great interest to compare the substrate properties of the oxygen and thiol analogues of esters with a cyclic ammonium group[63,66]. Table 5 lists the kinetic parameters of the cholinesterase hydrolysis of carboxylic acid thioesters. Two groups of compounds attract attention in the first place: the morpholine derivatives (XLIX)–(LII) and the α-pipecoline derivatives (LIII)–(LVI). Like the choline esters (Table 2), the acetates (XLIX) and (LIII) are hydrolysed at the highest rate by ACE. However, whereas BuTC is not hydrolysed by ACE, among the morpholinium derivatives the butyrate is hydrolysed, albeit 20 times more slowly than the acetate. Furthermore, the valerate is also hydrolysed at an appreciable rate. On the other hand, the change in the catalytic activity of BuCE following an increase in the bulk of the acyl component is different from that in the choline esters. Among the morpholinium derivatives, the propionate (L) is hydrolysed at the highest rate, while among the α-pipecolinium derivatives the rate of hydrolysis of the acetate (LII) is highest. Hence it follows that the dependence of the susceptibility of esters to cholinesterase hydrolysis as a function of the increase in the bulk of the acyl component of the molecule depends on the nature of the onium group.

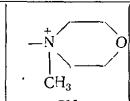
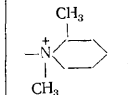
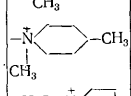
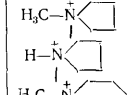
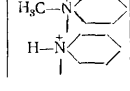
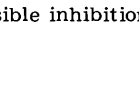
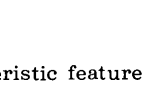
The hydrolysis by both enzymes of the protonated forms of the bases of the cyclic aminoalcohol esters (LX) and (LXII), in contrast to their oxygen analogues (see above), is of interest. Comparison of the values of a_C listed in Table 5 for the thioesters and those for their oxygen analogues (Table 4) reveals a definite regularity: when O is replaced by S, the rate of hydrolysis by BuCE either does not change or increases. The thio-substrates investigated therefore exhibit a lower specificity in relation to ACE. As shown below (Table 8), the replacement of O by S, as in the substrates (XXXII) and (XXXVII) resulted in a sharp decrease of specificity.

3. Esters of Cation-Containing Heterocycles

Table 6 lists the available comparative literature for the acetoxy-derivatives of ammonium-containing heterocycles as BuCE and ACE substrates. In contrast to all the compounds described above, the acyl residue in these esters is linked to

the onium nitrogen via a ring. The pyridinium derivatives (XXX)–(XXXV) are of great interest[67]. Despite the significant structural differences indicated, the rule that BuCE is more sensitive to changes in the alcohol component of the ester compared with ACE is valid for these compounds too. Thus a change in the position of the acetoxymethyl group in the methylated derivatives (XXX)–(XXXII) reduces sharply the rate of enzyme hydrolysis by BuCE but does not affect the hydrolysis by ACE. This was also observed for the ethylated derivatives (XXXIII) and (XXXIX). The high specificity of compound (XXXII) in relation to ACE is noteworthy.

Table 5. The interaction of the thioesters $RC(O)S(CH_2)_2R'$ with BuCE and ACE[63,66].

Compound	R	R′	BuCE		ACE	
			a_c, min^{-1}	K_M, mol litre^{-1}	a_c, min^{-1}	K_M, mol litre^{-1}
(XLIX)	CH_3		$6.6\cdot10^3$	$1.8\cdot10^{-4}$	$2.3\cdot10^4$	$6.0\cdot10^{-5}$
(L)	C_2H_5		$2.3\cdot10^4$	$8.9\cdot10^{-5}$	$1.6\cdot10^4$	$2.5\cdot10^{-4}$
(LI)	C_3H_7		$3.7\cdot10^3$	$7.8\cdot10^{-5}$	$1.2\cdot10^3$	$2.1\cdot10^{-4}$
(LII)	C_4H_9		$1.9\cdot10^3$	$1.9\cdot10^{-4}$	$8.8\cdot10^2$	$6.7\cdot10^{-4}$
(LIII)	CH_3		$3.6\cdot10^3$	$4.8\cdot10^{-4}$	$2.9\cdot10^4$	$2.4\cdot10^{-5}$
(LIV)	C_2H_5		$1.8\cdot10^3$	$4.8\cdot10^{-4}$	$4.4\cdot10^2$	$2.5\cdot10^{-4}$
(LV)	C_3H_7		$2.2\cdot10^2$	$8.3\cdot10^{-5}$	0	$1.4\cdot10^{-5}$ *
(LVI)	C_4H_9		0	$1.6\cdot10^{-3}$ *	0	$1.8\cdot10^{-5}$ *
(LVII)	CH_3		$1.1\cdot10^4$	$7.1\cdot10^{-5}$	$1.3\cdot10^4$	$7.4\cdot10^{-5}$
(LVIII)	C_2H_5		$2.5\cdot10^4$	$6.3\cdot10^{-5}$	$8.5\cdot10^3$	$4.0\cdot10^{-4}$
(LIX)	CH_3		$1.8\cdot10^4$	$5.3\cdot10^{-5}$	$1.4\cdot10^5$	$3.3\cdot10^{-5}$
(LX)	CH_3		$2.8\cdot10^3$	$1.2\cdot10^{-4}$	$7.0\cdot10^4$	$4.3\cdot10^{-4}$
(LXI)	CH_3		$4.4\cdot10^3$	$2.8\cdot10^{-5}$	$4.2\cdot10^4$	$2.4\cdot10^{-4}$
(LXII)	CH_3		$4.8\cdot10^2$	$2.4\cdot10^{-3}$	$1.4\cdot10^4$	$3.0\cdot10^{-4}$

* The reversible inhibition constant K_i is quoted.

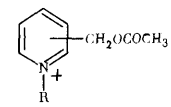
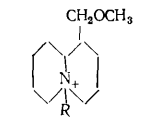
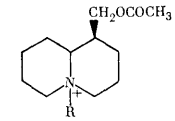
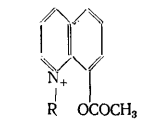
A characteristic feature of the lupinine and epilupinine derivatives (XXXVI) and (XXXVII) is that both cholinesterases are insensitive to epimeric transformations, but ACE hydrolyses these esters faster than BuCE[52,68].

Quinolinium derivatives have found extensive applications in laboratory practice. Table 6 presents data solely for 8-acetoxyquinolinium (XXXVIII)[69]. Other derivatives have been investigated only with ACE from the electric organ of *Torpedo mormorato* [? *Electrophorus electricus*][70,71]. The rate of hydrolysis of compound (XXXVIII) can be determined with a high accuracy by colorimetric and fluorimetric methods. It is hydrolysed by ACE at an even higher rate than AC.

IV. ESTERS OF ALIPHATIC AND AROMATIC ALCOHOLS

As early as 1949, it was established that cholinesterases are capable of hydrolysing not only the esters of cationoid alcohols but also the carboxylic acid esters of aliphatic alcohols[72–74]. Although the rates of hydrolysis were low, this fact was of fundamental importance. As for choline esters, on increase of the length of the acyl component of the molecule from the acetate to the butyrate, their rate of hydrolysis by ACE decreases while the rate of hydrolysis by BuCE increases. As regards the alcohol component, the carbon chain made up of four atoms is optimal for both enzymes. The branching of the alkyl chain has a major influence. The most complementary alkyl group for both cholinesterases is the 3,3-dimethylbutyl group, which is regarded as a carbon analogue of choline.

Table 6. The relative rates of hydrolysis v of the acetoxy-derivatives of certain ammonium-containing heterocycles by BuCE and ACE[72–74].

Compound	R	Position of CH_3OCOCH_3	Heterocycle	v*	
				BuCE	ACE
(LXIII)	CH_3	2		55	50
(LXIV)	CH_3	3		20	60
(LXV)	CH_3	4		3	50
(LXVI)	C_2H_5	2		125	35
(LXVII)	C_2H_5	4		10	35
(LXVIII)	C_3H_7	2		50	35
(LXIX) **	CH_2	—		7	21
(LXX)	CH_3	—		8	22
(LXXI)	CH_3			55	140

* The rate of hydrolysis of AC was adopted as 100.
** (LXIX) is lupinine, (LXX) is epilupinine, and (LXXI) is 8-hydroxyquinoline.

Carboxylic acid esters of aromatic hydroxy-compounds are frequently used in laboratory practice, namely those of phenol[75], nitrophenols, naphthols, and indole[76,77]. The esters of these aromatic alcohols are hydrolysed at a higher rate by cholinesterases. A whole series of resorufin and anthracene derivatives have been proposed for a highly sensitive fluorimetric method for the determination of cholinesterase activity[77].

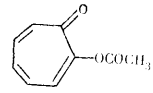
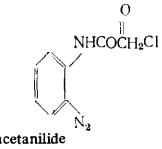
Carboxylic acid esters of indophenol and its halogeno-derivatives occupy a special place among non-cationoid substrates[4,78]. They are widely used in colorimetric methods for the determination of the cholinesterase activity not only with the aid of instruments but also visually. This is because the esters have a pale-red colour and their hydrolysis products (indophenols) are intensely blue. It is striking that ACE hydrolyses only the unsubstituted indophenyl ester, while BuCE hydrolyses also the halogeno-derivatives.

All the esters enumerated in this Section suffer from an important disadvantage: in contrast to the choline esters, they are readily hydrolysed by other esterases. In order to determine the cholinesterase activity of biological tissues with the aid of such chromogenic substrates, one finds initially the overall esterase activity and then, after treating

the tissue with a specific CE inhibitor, the esterase activity is remeasured. The difference between these two measurements characterises the activity of cholinesterases.

It should be noted particularly that certain types of cholinesterases do not hydrolyse all chromogenic substrates: the CE from the nerve ganglia of the cockroach do not hydrolyse *p*-nitrophenyl acetate, which is used to determine the activities of the carboxy-esterases of this insect[79].

Table 7. The hydrolysis of new non-cationogenic substrates by the ACE from the electric organ of *Torpedo mormorato* [?*E. electricus*].

Compound	Substrate	a_c, min^{-1}	K_M, mol $litre^{-1}$
(LXXII)	AC	$9.8 \cdot 10^5$	0.4
(LXXIII)	vinyl acetate $CH_2 = CHOC(O)CH_3$	$10.5 \cdot 10^5$	67.0
(LXXXIV)	but-1-enyl acetate $CH_3CH_2CH = CHOC(O)CH_3$	$5.7 \cdot 10^5$	1.1
(LXXV)	propylidene diacetate $CH_3CH_2CH(OCOCH_3)_2$	$6.0 \cdot 10^5$	1.7
(LXXVI)	benzylidene diacetate $C_6H_5CH(OCOCH_3)_2$	$6.6 \cdot 10^5$	1.5
(LXXVII)	 tropolone acetate	$10.2 \cdot 10^5$	0.55
(LXXVIII)		$1.6 \cdot 10^4$	2.5
(LXXIX)	*o*-nitrochloroacetanilide *o*-nitrodichloroacetanilide	$1.2 \cdot 10^4$	0.6

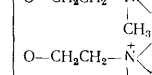
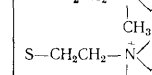
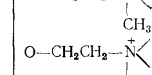
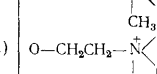
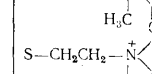
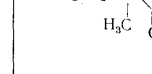
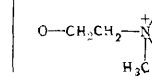
New unusual substrates of the ACE from the electric organ of *Torpedo mormorato* [? *Electrophorus electricus*] have been investigated recently[80]. Table 7 shows that these non-cationoid esters are hydrolysed by ACE a little less effectively than AC, while tropolone acetate (LXXVII) is actually more effectively hydrolysed. The alkylidene diacetates (LXXV) and (LXXVI), where the 2-acetoxy-groups are attached to a single carbon atom, are of interest. The usual dicarboxylic acid esters of dihydric alcohols are slowly hydrolysed by cholinesterases. For example, the hydrolysis of 9,10-diacetoxyanthracene by BuCE is much slower than that of 9-acetoxyanthracene, i.e. the second acetoxy-group interferes with the enzymic reaction[77]. In contrast to such dicarboxylic acid esters, alkylidene diacetates are hydrolysed by the ACE from the electric organ of *Torpedo mormorato* [? *Electrophorus electricus*] only 1.5 times more slowly than AC. One cannot rule out the possibility that the enzyme hydrolysis of the first acetoxy-group is followed by the spontaneous hydrolysis of the second. The possibility of the cholinesterase hydrolysis of the amide bond was demonstrated in the same study in relation to the non-cationoid acetanilides (LXXVI) and (LXXIX).

V. CONCLUSION

The data presented in this review indicate a limited specificity of the catalytic activity of ACE and BuCE. Both enzymes are capable of hydrolysing an extremely large number of choline and non-choline carboxylic acid esters. The difference between the specificities of these enzymes consists in the fact that ACE is more sensitive to the structure of the acid component of the esters, while BuCE is more sensitive to the structure of the alcohol component. It has been shown that ACE and BuCE are stereospecific in relation to optical isomers. Both enzymes are sensitive to the optical isomers of substrates in which the asymmetric carbon atom is in the β-position with respect to the choline component of the molecule. Furthermore, ACE is capable of distinguishing between the optical isomers of substrates in which the asymmetric carbon atom is in the acid component.

Apart from the specificity of the catalytic activity of cholinesterases, there exists also the concept of specific substrates. A specific substrate for a given enzyme is believed to be one whose rate of reaction under the influence of the given enzyme is greater by a factor of tens than the rate of its reaction under the influence of another enzyme. The specificity of the substrate can vary appreciably as a function of the enzymic process conditions: pH, ionic strength, and particularly substrate concentrations. As shown above, at high concentrations of the substrate its specificity with respect to the two cholinesterases is determined by the ratio $a_{c,1}/a_{c,2}$, while at low concentrations it is determined by the ratio $(a_c/K_M)_1/(a_c/K_M)_2$. Until recently only BuC and BeC for BuCE and AMC for ACE were believed to be specific substrates for these enzymes. The study of the acetates of cyclic aminoalcohols led to the discovery of several specific ACE substrates with a more pronounced selectivity (Table 8).

Table 8. The specificity of the acetates $CH_3C(O)X$ to ACE[48,81].

Compound	X	$\frac{a_c\ (ACE)}{a_c\ (BuCE)}$	$\frac{(a_c/K_M)\ (ACE)}{(a_c/K_M)\ (BuCE)}$
(XX)	$O-CH_2CH_2\overset{+}{N}(CH_3)_3$	5	12
ATC	$S-CH_2CH_2\overset{+}{N}(CH_3)_3$	2	11
(LXIII)	$O-CH(CH_3)CH_2\overset{+}{N}(CH_3)_3$	30	32
(LXIV)	$S-CH(CH_3)CH_2\overset{+}{N}(CH_3)_3$	3	10
(XXX)		20	15
(XXXIII)		65	5
(LXI)		10	1
(XXXVII)		50	30
(XXXVIII)		35	18
(LIII)		8	160
(XLII)		35	40

The most specific ACE substrates at high ester concentrations (in terms of the ratio of the parameters a_c) are compounds (XXXIII) and (XXXVII), for which the ratios are 65

and 50 and which are greatly superior to AMC as regards this parameter (the ratio of the a_C is 30).

The esters (XXXVII) and (XLII) proved to be highly specific ACE substrates at both high and low concentrations. Among the newly discovered specific substrates, the derivatives of piperidine (XXXIII) and morpholine (XXXVII) are widely used in laboratory practice.

As stated above, the thio-analogues of AC and AMTC exhibit a lower specificity in relation to ACE. This has been confirmed also for the piperidine derivatives (LII) and (LIII). As regards the α-pipecoline analogues (XXXVIII) and (LIII), the specificity fell only when their concentrations were high, while at low concentrations the specificity (the a_C/K_M ratio) increased sharply. The thioester (LXI) is so far the only thio-substrate which can be regarded as specific to ACE[63,66].

The data presented in this review, indicating an extremely high sensitivity of BuCE to changes in the structure of the ammonium group of the substrate, suggest that the dimensions of the anionic centre in BuCE are limited[48,81]. Presumably in the region of the anionic centre there is a pit whose shape and dimensions determine the limiting structures of the cationic group of such a substrate for which hydrolysis is still possible. Theoretical conformational analysis of AC derivatives with different structures of the ammonium group has shown that the substrate molecule exists in the form of a mixture of conformations separated as a rule by high potential barriers. If the substrate interacting with BuCE has a conformation whose dimensions exceed the limiting size of the pit in the anionic centre, non-productive sorption of the substrate takes place. The conformations of the ester in which the cationic group fits within the limits of the anionic centre of BuCE are susceptible to hydrolysis. Accordingly, the conformations of the same substrate can be divided into productive and non-productive. The analysis carried out here has demonstrated a very satisfactory correlation between the relative populations of the productive conformations of substrates and the rate of hydrolysis by BuCE.

At first sight it would seem that an increase in the size of the *N*-alkyl group should hinder sorption in the region of the anionic centre and hence reduce the rate of hydrolysis by BuCE. However, according to the results of theoretical conformational analysis, conformers with a more compact packing of the alkyl groups than in the propyl derivative (XXII) are characteristic of the pentyl derivative (XXIV).

Thus it is possible to explain the "anomalous" variation of the rate of hydrolysis in the sequence (XX), (XXII), and (XXIV); compound (XXII) is hydrolysed less effectively by factors of 3 and 2.5 than compounds (XX) and (XXIV) respectively. This can also be said of the *N*-alkylpiperidinium derivatives (XXXII), (XXXIV), and (XL), among which the isopropyl analogue (XL) proved to be more compact than the methyl derivative (XXXIII).

This new approach leads to the possibility of investigating the characteristics of the structure of the catalytic surface of cholinesterases by substrate analysis and permits direct recommendations for the synthesis of highly specific substrates.

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Advances in the Chemistry of σ-Derivatives of Group IVB–VIB Transition Metals

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A systematic account is given of the literature data on the methods of synthesis and reactivities of transition metal σ-derivatives R_nM and R_nMX_{m-n} (X = halogen, OR′, acac, or NR'_2; R′ = Me, Et, or Ph; n = valence of the metal) for transition metals in the Ti, V, and Cr subgroups. The influence of the nature of the central atom and of the character of the σ-substituents on the mode of thermal decomposition is discussed. The mechanisms of reactions involving insertion in the transition metal-carbon σ-bond are considered.
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I. INTRODUCTION

The chemistry of organometallic compounds (OMC) involving transition metals is at present one of the most rapidly and successfully developing branches of coordination chemistry.

The beginning of the development of the chemistry of σ-derivatives of transition metals was associated with attempts to obtain compounds of the type R_nM (R = Me, Et, or Ph; M = metal; n = valence of the metal), which were known for non-transition elements. The failure of these attempts led Krause and Grosse to postulate in 1937, in their detailed monograph on OMC chemistry, that transition metals with *d* orbitals cannot form a σ-bond with carbon.

However, studies carried out in the 1950's–1960's showed that R_nM (R = Me, Et, or Ph) derivatives of transition metals exist in solutions at low temperatures, decomposing when the temperature is increased. The results led to the erroneous hypothesis that the transition metal–carbon σ-bond is weak and that σ-derivatives of the type R_nM cannot be isolated. At this time attention was therefore concentrated on the study of the thermally stable complexes $R_nM.xL$ containing "stabilising" ligands such as CO, PR_3, or π-C_5H_5(Cp). The existing theory of the stability of the transition metal–carbon σ-bond postulated that the role of these ligands consists in increasing the energy of the σ-bond. However, subsequent numerous experimental data and their theoretical analysis demonstrated that the transition metal–carbon σ-bond is not weak. In his report at the Vth International Congress on Organometallic Chemistry, Wilkinson justified the view generally accepted at the present time; the thermal instability of the R_nM σ-derivatives is due to their kinetic instability associated with the low activation energy for the decomposition reaction. Since one of the main pathways leading to the decomposition is elimination of the alkene as a result of the transfer of a β-hydrogen atom to the metal atom, the compounds R_nM with σ-substituents which do not contain β-hydrogen atoms should be kinetically stable. Such substituents include the benzyl, neopentyl, trimethylsilylmethyl, mesityl, methyladamantyl, and other groups. The introduction of the electronegative perfluoroalkyl or perfluorophenyl σ-substituents into the molecule increases the activation energy for the decomposition reaction. In addition, it has been established that the successful isolation of the compounds R_nM depends on the correct choice of the method and conditions of the synthesis[1–4].

On the basis of the principles of kinetic stability, major advances have been achieved during the last decade on the isolation of individual σ-derivatives of transition metals of the type R_nM or R_nMX_{m-n} [X = halogen (Hal), OR′, acac, or NR'_2; R′ = alkyl or aryl]. They are as a rule extremely sensitive to oxygen and moisture but, in the absence of the latter, can exist for a long time at room temperature in the solid state or in solution without decomposition.

The reactivity of the transition metal–carbon σ-bond is being vigorously investigated. Attention has been concentrated on insertion reactions which take place in many catalytic processes. Instead of the compounds R_nM, many investigators have frequently used in the study of these reactions cyclopentadienyl derivatives of the type $Cp_2M(\sigma\text{-}R)_z$ (R = Me, Ph, CH_2Ph, or C_6H_5; z = 1 or 2) instead of the compounds R_nM. They are convenient objects of study, since the Cp_2M group is not involved in the reactions and the insertion products are fairly easy to identify.

The latest advances in the synthesis, isolation, and investigation of the chemical properties of individual σ-derivatives of Group IVB–VIB transition metals of the type R_nM or R_nMX_{m-n} (R = CH_2Ph, CH_2SiMe_3, CH_2CMe_3, Mes, adme, or C_6F_5; X = Hal, OR′, acac, NR'_2; R′ = alkyl or aryl; n = the valence of the metal; $m > n$)† will be examined in this review. The results of studies on the σ-derivatives of manganese, iron, cobalt and nickel as well as $Cp_2M(\sigma\text{-}R)_2$ will be resorted to in some cases in the discussions of the reactivity of the transition metal–carbon σ-bond.

II. THE SYNTHESIS OF σ-DERIVATIVES OF TRANSITION METALS

The main method of synthesis of the σ-derivatives involves the reaction of transition metal salts with organometallic compounds of lithium, magnesium, and zinc and, more rarely, mercury and aluminium. All these syntheses are usually carried out at low temperatures and with careful elimination of oxygen and moisture. The choice of the solvent has an appreciable influence on the yield of the product. The

† Mes = mesityl, adme = adamantylmethyl, and acac = acetylacetonate.

Table 1. Benzyl derivatives R_nM ($R = CH_2Ph$).

R_nM	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MX_n	R_nE	solvent	t, °C		m.p., °C	colour	
R_4Ti	$TiCl_4$	RMgCl	Et_2O	−20	40	71	dark-red	[5]
R_4Zr	$ZrCl_4$	RMgCl	Et_2O	−20	30	134	yellow	[5]
R_4Hf	$HfCl_4$	RMgCl	Et_2O	−90	60	114	pale-yellow	[6]
R_4V	VCl_4	R_2Mg	Et_2O	−70	25	80[a]	black-green	[9, 10]
R_5Ta	R_3TaCl_2	R_2Mg	toluene	−70	93	—[b]	red	[12]
R_4Cr[c]	$CrCl_3 \cdot 3THF$	RLi	THF + benzene	−20	5	—[e]	red-brown	[13]
R_4Mo	$MoCl_4 \cdot 2Et_2O$	R_2Mg	Et_2O	−40	75[d]	75[d]	black-brown	[15]
R_4W	$WCl_4 \cdot 3THF$	R_2Mg	Et_2O	−20	40	90[d]	red-brown	[14]
R_3Ti[c]	R_3Ti	EtLi	xylene	0	93	—	yellow	[18]
R_3V[c]	$VCl_3 \cdot 3THF$	RLi	THF	−70	88	—	blue	[21]
$R_2Ti \cdot 3Et_2O$	Cp_2TiR_2	RLi	Et_2O	+20	40	200[d]	black	[22]

Remarks: [a] melts with decomposition; [b] m.p. not determined; [c] obtained in solution; [d] decomposes without melting; [e] yield not indicated.

alkylating agents cannot always be interchanged. The most reactive alkylating agents are organolithium compounds. With their aid and at fairly low temperatures, it is possible to obtain fully substituted derivatives R_nM. It is noteworthy that, when organolithium compounds are used, it is necessary to maintain rigorously the stoichiometry of the reactions, since an excess of the organolithium compound entails the formation of ate-complexes, which reduces the yield and hinders the isolation of R_nM in a pure form.

The magnesium derivatives RMgHal and R_nMg are most widely used as alkylating agents as a result of their ready availability. However, when RMgHal is employed, the transition metal is sometimes reduced owing to the presence in the reaction mixture of the partly soluble $MgCl_2$, which forms relatively unstable complexes with R_nM. To prevent this process, dioxane, which binds magnesium chloride in the insoluble complex $MgCl_2$.diox, is added to the reaction mixture. Virtually complete separation of $MgCl_2$ from R_nM, which remains preferentially in solution, is then achieved. Organozinc compounds behave as mild alkylating agents. They do not reduce the transition metal, but, even in the presence of an excess of R_2Zn, the complete alkylation of MX_n is not observed. They are therefore used successfully for the synthesis of alkyl(aryl)metal halides R_nMHal_{m-n} ($n = 1, 2, 3$; $m = 4, 5$).

The metal chlorides and their complexes with Et_2O or tetrahydrofuran (THF) are usually employed as the transition metal compounds. In some cases it is desirable to use metal alkoxides, which are more soluble in organic solvents than the corresponding halides.

Thus the decisive factors for the isolation of individual R_nM are the character of the initial transition metal compound and the alkylating agent, the reaction stoichiometry, the absence of Lewis acid impurities from the reaction mixture, and the nature of the solvent. In the present review the above factors were chosen as the basis for the discussion of various methods of synthesis of the σ-derivatives. In each Section the compounds are grouped in terms of types of σ-substituents and in each Subsection compounds of the highest valences of Group IV–VII metals are considered initially and then compounds of the lowest valences of the metals in the same sequence within the Groups.

1. Synthesis of R_nM

Benzyl Derivatives (Table 1)

The tetrabenzyl derivatives of metals of the titanium subgroup have been synthesised by the classical procedure—the double decomposition reaction of the metal chloride with a Grignard reagent in ether at a low temperature[5,6].

In contrast to this, the double decomposition reaction of VCl_4 with $PhCH_2MgCl$ is accompanied by a decrease of the valence of vanadium regardless of the initial reactant ratio, the nature of the solvent, and temperature[7]. The optimum method of synthesis of $(PhCH_2)_4V$ proved to be the reaction of VCl_4 with $(PhCH_2)_2Mg$ in Et_2O at −70 °C.[8–10] The benzyl derivatives of niobium have not so far been obtained. Benzylation of $NbCl_n$ ($n = 5, 4$) not only with a Grignard reagent but also with $(PhCH_2)_2M$ (M = Mg, Zn, or Hg) was accompanied by the formation of complexes of low-valence niobium[11]. Similarly, in the benzylation of $TaCl_5$ by $(PhCH_2)_2Mg$, tantalum(V) was reduced[12]. However, by selecting the appropriate conditions of synthesis, it was possible to obtain $(PhCH_2)_5Ta$. $TaCl_5$ is initially treated with $(PhCH_2)_2Zn$, which does not reduce the transition metal. The reaction results in the isolation of the mixed derivative $(PhCH_2)_3TaCl_2$. The subsequent substitution of the residual chlorine atoms by benzyl groups takes place under the influence of $(PhCH_2)_2Mg$ in toluene. The employment of toluene and the addition of dioxane enabled the authors to eliminate $MgCl_2$ completely from the reaction zone and to obtain $(PhCH_2)_5Ta$ in an almost quantitative yield[12].

The compound $(PhCH_2)_4Cr$ has been obtained only in solution and has been identified by its EPR spectrum[13]. The influence of the conditions of synthesis on the formation of the benzyl derivatives of molybdenum and tungsten has been studied in detail. It has been established that the tetrabenzyl derivatives of molybdenum and tungsten can be isolated as a result of the interaction of $MoCl_4.2Et_2O$ and $WCl_4.2THF$, which are readily soluble in ether, with $(PhCH_2)_2.Mg$.[14,15]

Organic σ-compounds of tervalent metals are known only for titanium, vanadium, and chromium. The probable explanation is that the initial low-valence derivatives are difficult to obtain for the remaining Group IV–IVB metals.

Table 2. Neopentyl and trimethylsilylmethyl derivatives R_nM and R'_nM ($R = CH_2CMe_3$; $R' = CH_2SiMe_3$).

R_nM, R'_nM	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MX_n	RE, R'E	solvent	t, °C		colour	m.p., °C	
R_4Ti	$TiCl_4$	RLi	hexane	—70	26	yellow	105[a]	[24, 25]
R_4Zr	$ZrCl_4$	RLi	hexane + Et_2O	0	68	colourless	108[a]	[24, 25]
R_4Hf	$HfCl_4$	RLi	hexane + Et_2O	0	59	colourless	115	[24, 25]
R_4Cr	$CrCl_3 \cdot 3THF$	RMgCl	Et_2O	+20	30	chestnut	110	[13]
$R_4'Ti$	$TiCl_4$	R'MgCl	Et_2O	—20	65	yellow	+1	[26]
$R_4'Zr$	$ZrCl_4$	R'Li	Et_2O	0	89	colourless	10	[26]
$R_4'Hf$	$HfCl_4$	R'Li	hexane + Et_2O	0	96	colourless	10	[26]
$R_4'V$	VCl_4	R'Li	hexane	—60	10	green	42	[27]
$R_4'Cr$	$CrCl_3 \cdot 3THF$	R'MgCl	Et_2O	20	30	purple	40	[27]
R'_3Ti[b]	$R_4'Ti$	R'Li	toluene	0	50	yellow	—	[18]
$R'_3V.THF$	$VCl_3 \cdot 3THF$	R'MgCl	THF	—60	60	violet	75	[21]
$R_2'Cr$	$CrCl_3$	R'Li	hexane	20	97	dark violet	—[c]	[33]

Remarks: [a] melts with decomposition; [b] obtained in solution from R'_4Ti and EtLi; [c] m.p. not determined.

The possibility of synthesising $(PhCH_2)_3Ti$ by several procedures has been investigated. The double decomposition reaction of $TiCl_3.3THF$ or $Ti(acac)_3$ with an organomagnesium compound in Et_2O at −30 °C results in the formation of $(PhCH_2)_3Ti$. The attempts to isolate this compound lead to its decomposition at 0 °C.[16,17] Success was achieved by another method of synthesis involving the decomposition of ate-complexes:

$$(PhCH_2)_4Ti + EtLi \xrightarrow[0°C]{\text{xylene}} [(PhCH_2)_4\,TiEt]^-Li^+ \rightarrow$$
$$\rightarrow [(PhCH_2)_3TiEt] + PhCH_2Li$$
$$\downarrow \qquad\qquad CO_2\downarrow -78°C$$
$$(PhCH_2)_3Ti + [Et^\cdot]\ PhCH_2CO_2Li\ .$$

However, it has not so far been possible to isolate $(PhCH_2)_3Ti$ in a pure form; $(PhCH_2)_3Ti$ has only been obtained in the form of solutions in aromatic hydrocarbons[18,19].

The benzylation of $VCl_3.3THF$ or $V(acac)_3$ by $PhCH_2MgCl$, $(PhCH_2)_2Mg$, and $(PhCH_2)_3Al$ in Et_2O does not go to completion[17,20]. The reaction of $VCl_3.3THF$ with three moles of $PhCH_2Li$ in THF results in a complete exchange of chlorine atoms for benzyl groups. However, $(PhCH_2)_3V$ could not be isolated in a pure form: at 0 °C the compound decomposes rapidly in solution[21].

The attempts to synthesise $(PhCH_2)_3Cr$ have so far been unsuccessful[17].

Among the benzyl derivatives of bivalent metals, only $(PhCH_2)_2Ti.3Et_2O$ has so far been isolated; it is obtained on decomposition of the ate-complex formed from $Cp_2Ti(CH_2Ph)_2$ and $PhCH_2Li$.[22] The complex $(PhCH_2)_2Ti.3diox$ has been obtained by the oxidative-reduction symmetrisation of benzyl derivatives of titanium(III).[23]

The Neopentyl and Trimethylsilylmethyl Derivatives (Table 2)

These substituents belong to the single type CH_2EMe_3 (E = C, Si, Ge, or Sn) and are more bulky than the benzyl derivatives.

The neopentyl derivatives of the titanium subgroup are obtained by the double decomposition reaction of the metal halides MCl_4 with Me_3CCH_2Li.[24,25] The trimethylsilylmethyl derivatives of the titanium subgroup metals are formed as a result of the reaction of MCl_4 with both a Grignard reagent and an organolithium compound. It has been established that the best alkylating agent for $ZrCl_4$ and $HfCl_4$ is Me_3SiCH_2Li. A high yield of $(Me_3SiCH_2)_4M$ (M = Ti, Zr, or Hf) is achieved in the presence of a 5% excess of MCl_4. When the initial reactant ratio is exactly 1 : 4, the complexes $(Me_3SiCH_2)_4M.(Me_3SiCH_2)_2Mg$, which are difficult to separate, arise in the reaction mixture, while in the presence of an excess of MCl_4 greater than 5% the stable compounds $(Me_3SiCH_2)_3MCl$ are produced.[26]

Among the neopentyl and trimethysilylmethyl derivatives of the Group VB metals, only $(Me_3SiCH_2)_4V$ has been isolated[27]. It has been established that the preparation of niobium and tantalum derivatives is hindered by steric factors. When attempts were made to synthesise $(Me_3ECH_2)_5M$, the alkylidene or alkylidyne complexes of these metals were isolated[25,28,29]. It was possible to synthesise the compound $Me_3Ta(CH_2SiMe_3)_2$, since the small methyl substituents are distributed in its molecule around the Ta atom, together with the Me_3SiCH_2 groups[30].

Virtually the same features have been observed for the metals of the chromium subgroup as for the Group VB metals. The interaction of the ether-soluble $CrCl_3.3THF$ with four equivalents of Me_3ECH_2MgCl (E = C or Si) under identical conditions yields the tetrasubstituted derivatives $(Me_3ECH_2)_4.Cr$ (E = C or Si) with identical yields[13,27]. The reactions of molybdenum and tungsten halides ($MoCl_5$ and WCl_5) with Me_3SiCH_2MgCl in Et_2O at 20 °C result in the formation of the dimeric bridged complexes $(Me_3SiCH_2)_6M_2$.[27] An analogous complex with neopentyl ligands has been obtained from $MoCl_5$ and Me_3CCH_2Li in Et_2O at 20 °C;[25] after the exchange of all the chlorine atoms in WCl_6 for the neopentyl groups, the carbyne complex $(Me_3CCH_2)_3W(\equiv C-CMe_3)$ is obtained from WCl_6 with the aid of Me_3CCH_2Li.[31]

The trimethylsilylmethyl derivatives of tervalent titanium and vanadium have been synthesised. The compound $(Me_3SiCH_2)_3Ti$ has been obtained in solution in toluene on decomposition of the ate-complex $[(Me_3SiCH_2)_4TiEt]^-Li^+$.[18]

After the alkylation of $VCl_3.3THF$ with Me_3SiCH_2MgCl, the complex $(Me_3SiCH_2)_3V.THF$, which is stable at room temperature, was isolated in a pure state[21]. It has been established that the successful alkylation of $VCl_3.3THF$ depends on the nature of the solvent and temperature.

A considerable stabilisation of the tervalent states is attained when the substituents $(Me_3Si)_2CH$ are used. The reaction of $[(Me_3Si)_2CH]Li$ with a suspension of MCl_3 in Et_2O at −60 °C afforded low yields of the derivatives $[(Me_3Si)_2CH]_3M$ (M = Ti, V, or Cr).[32] An interesting fact has been observed in relation to vanadium—the coordination number of the metal depends on the bulk of the substituent: tricoordinate compounds are obtained with the bulky substituent $(Me_3Si)_2CH$, while tetracoordinate derivatives are isolated with the less bulky substituent Me_3SiCH_2.

Among the bivalent Group IV–IVB metal derivatives, only $(Me_3SiCH_2)_2Cr$ has been described hitherto. On the other hand a quadrivalent chromium derivative R_4Cr is obtained

Table 3. Mesityl, 1-methyladamantyl, and pentafluorophenyl derivatives (R = Mes; R′ = 1-adme; R″ = C_6F_5).

R_nM, R'_nM, R''_nM	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MX_n	reagent	solvent	t, °C		colour	decomp. temp. °C	
R_4Ti	$[R_4Ti]Li$	O_2	—	20	—[a]	chrome-yellow	159	[34]
R_4V	$[R_4V]Li$	O_2	Et_2O + THF	20	90	dark-red	152	[35]
R_4Cr	$[R_4Cr]Li$	O_2	Et_2O	20	56	dark-brown	110	[36]
R_4Mo	$[R_4Mo]Li$	O_2	Et_2O	20	90	black-green	276	[37]
$R_3V.THF$	$VCl_3 \cdot 3THF$	RMgBr	THF	—30	45	blue	125	[39]
$R_3Cr.3THF$	$CrCl_3$	RMgBr	THF	—20	a	dark blue	80	[40]
$R_2Cr.3THF$	$CrCl_2$	RMgBr	THF	0	25	violet	50	[41]
$R_4'Ti$	$Ti(OPr\text{-}iso)_4$	R′Li	PE	—20	60	yellow	145	[43]
$R_4'Zr$	$ZrCl_4$	R′MgBr	Et_2O	—50	39	cream	130	[43]
$R_4'V$	$V(OPr\text{-}iso)_4$	R′Li	PE	—60	54	blue-green	80	[43]
$R_4'Cr$	$Cr(OBu\text{-}t)_4$	R′Li	PE	—60	45	chestnut	164	[43]
$R_4''Ti \cdot Et_2O$	$TiCl_4$	R″MgBr	Et_2O + hexane	—70	30	orange	119	[44]
$R_4''Zr \cdot Et_2O$	$ZrCl_4$	R″Li	Et_2O + hexane	—70	73	yellow	100[b]	[45]
$R_4''V \cdot 2Et_2O$	VCl_4	R″Li	Et_2O + hexane	—70	70	violet	220[b]	[46]
$R_3''Ti.3THF$	$TiCl_3.3THF$	R″MgBr	THF	0	45	dark-green	122[b]	[48]
$R_3''V.THF$	$VCl_3.3THF$	R″Li	THF	—70	85	brown	10	[21]

Remarks: [a] yield not indicated; [b] melts with decomposition; PE = petroleum ether.

when $CrCl_3.3THF$ is treated with an excess of RLi or RMgCl (R = CH_2Ph or CH_2EMe_3),[13,27] while the reaction of $CrCl_3$ with a deficiency of Me_3SiCH_2Li results in the formation of $(Me_3SiCH_2)_2Cr$; the reaction mechanism has not been established[33].

The Mesityl Derivatives (Table 3)

The tetramesityl derivatives cannot be obtained by the usual double decomposition reaction between metal halides and a Grignard reagent or RLi. In view of the large bulk of the ligand, only three chlorine atoms are substituted in these reactions even in the presence of the arylating agents. A novel method of synthesis has been developed, consisting in the oxidation of the ate-complexes and the tervalent metals, which give rise to derivatives of the quadrivalent metals after careful choice of oxidation conditions[34–37]:

$$MCl_3 \cdot 3THF + 4MesLi \xrightarrow[20°C]{THF+Et_2O} [Mes_4M]^- Li^+ \cdot 4THF + 3LiCl$$
$$\downarrow \tfrac{1}{2}O_2$$
$$Mes_4M + LiO + 4THF$$

Derivatives of titanium, chromium, vanadium, and molybdenum have been obtained in this way. The difficulties in synthesising the tetramesityl derivatives of zirconium, hafnium, niobium, tantalum, and tungsten are associated with the fact that the initial MCl_3 are at present difficult to obtain.

Mesityl derivatives of tervalent metals have been obtained for vanadium and chromium. Unfortunately attempts to synthesise Mes_3Ti have not been described, although in the synthesis of Mes_4Ti the compound $TiCl_3.3THF$ was mesitylated[34]. Mes_3V was isolated in a pure form after the reaction of $VCl_3.3THF$ with three moles of MesMgBr, but not with MesLi, since interaction with the latter results in the preferential formation of the ate-complex of vanadium(III), rather than the neutral compound[38,39]. $Mes_3Cr.THF$, which cannot be converted into an arene complex because of the characteristic features of the mesityl group, proved to be easy to synthesise[40]. For the same reason, it has been possible to obtain and investigate the σ-mesityl derivatives of chromium(II).

The complex $Mes_2Cr.3THF$ can be obtained from anhydrous $CrCl_2$ and MesMgBr.[41] It is of interest that Mes_2Cr can give rise to complexes with coordination numbers ranging from 3 to 5. If the pentacoordinate complex $Mes_2Cr.3THF$ is dissolved in hexane at 20 °C. the colour of the solution changes, after 15–20 min from violet to green and a green deposit having the composition $Mes_2Cr.3THF$ is precipitated. Three molecules of the coordinated THF are readily substituted by one molecule of the bidentate bipyridyl ligand with formation of dark-blue crystals of the tetracoordinate chromium complex $Mes_2Cr.bipy$.[41] The formation of Mes_2Mo was unexpected; the authors[42] believe that the interaction of Mes_2MoO_2 with MeLi involves reduction:

$$Mes_2MoO_2 + 2MeLi \xrightarrow[0°C]{Et_2O} Mes_2Mo \cdot 2Et_2O + 2MeOLi$$

However, a change in the valence of molybdenum was not demonstrated analytically and the properties of this compound were not investigated.

The Adamantylmethyl Derivatives (Table 3)

The 1-adamantylmethyl (adme) ligand has a large bulk. It has been established that the peralkyl compounds R_nM incorporating this ligand decompose above 100 °C. In the synthesis of $(adme)_4M$ (M = Ti, V, or Cr), the alkoxides and not the halides were used as the initial transition metal compounds (the use of MCl_4 leads to an extremely low yield of the final products). The employment of soluble derivatives $M(OR)_4$ made it possible to carry out the reaction in saturated hydrocarbons at low temperature.

The compound $(adme)_4Ti$ crystallises in an analytically pure form from the $Ti(OPr\text{-}iso)_4$ + 4(adme)Li system in petroleum ether at 20 °C.[43] In view of the difficulty of obtaining the initial reagent $Zr(OPr\text{-}iso)_4$, $ZrCl_4$ was used in the synthesis of $(adme)_4Zr$. The isolation in a pure state of the compound $(adme)_4Zr$ obtained from $ZrCl_4$ and (adme)MgBr therefore requires repeated crystallisation in order to eliminate the admixture of magnesium halide salts[43].

Treatment of $V(OPr\text{-}iso)_4$ with an excess of (adme)Li gives the unexpected product $(adme)_4V$.[43] The attempts to obtain the peradamantylmethyl derivatives of niobium and tantalum ended in failure, whose only cause was the steric hindrance resulting from the disposition of the five bulky groups around the Nb and Ta atoms. Treatment of $Nb(OBu\text{-}t)_5$ with an excess of (adme)Li resulted in the formation of a mixture of the di- and tri-alkylated products. When $TaCl_5$ was allowed

Table 4. Benzylmetal halides R_nMHal_{m-n} ($R = CH_2Ph$; $n = 1, 2, 3$; $m = 4, 5$).

Benzylmetal halide	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	R_nM	reagent	solvent	t, °C		colour	m.p., °C	
R_3TiF	R_4Ti	BF_3 (gas)	toluene	—10	40	red-brown	100[a]	[5]
R_3TiCl	R_4Ti	HCl (gas)	toluene	—10	86	red-brown	100[a]	[5]
R_3TiBr	R_4Ti	HBr (gas)	toluene	—10	89	red	100[a]	[5]
R_3TiI	R_4Ti	I_2	toluene	—20	70	dark-red	—[b]	[50]
R_2TiBr_2	R_4Ti	$TiBr_3$	toluene	—10	60	red	80	[5]
R_3ZrCl	R_4Zr	HCl (gas)	toluene	—10	80	yellow	89	[5]
R_2ZrCl_2	R_4Zr	HCl (gas)	toluene	—10	60	orange-yellow	60[c]	[5]
$R_3TaCl_2 \cdot$ bipy	$TaCl_5$	R_2Zn	toluene	20	55	orange	—[b]	[12]
$R_2TaCl_3 \cdot$ bipy	$TaCl_5$	R_2Zn	PE	—50	—[d]	brown	110	[10]
R_3TaCl_2	$TaCl_5$	R_2Zn	hexane	20	—[d]	yellow-brown	—[b]	[10]
$RTaCl_4$	$TaCl_5$	R_2Mg	PE	20	—[d]	yellow-brown	—[b]	[10]

Remarks: [a] melts with decomposition; [b] m.p. not determined; [c] decomposes without fusion; [d] yield not indicated.

to react with (adme)MgBr in Et_2O, only three chlorine atoms were substituted with formation of $(adme)_3TaCl_2$.[43]

The Pentafluorophenyl Derivatives (Table 3)

These derivatives have a much higher thermal stability than the phenyl compounds. While the Ph_4M (M = Ti, Zr, or V) derivatives cannot be isolated in a pure state, the corresponding pentafluorophenyl compounds are stable on heating to 100 °C and above.

The compound $(C_6F_5)_4Ti$ can be isolated in the form of the hexacoordinate complex $(C_6F_5)_4Ti.2Et_2O$ as a result of the double decomposition reaction between $TiCl_4$ and C_6F_5MgBr.[44] The best alkylating agent for the zirconium salt proved to be C_6F_5Li. In contrast to the titanium compound, the σ-derivative of zirconium can be isolated in the form of the pentacoordinate complex $(C_6F_5)_4Zr.Et_2O$.[45]

The interaction of VCl_4 with C_6F_5Li leads to the formation of the complex $(C_6F_5)_4V.2Et_2O$.[46] A brief communication (without description of experimental conditions) concerning the synthesis of the light-sensitive and volatile compound $(C_6F_5)_4Nb$ has been published[47].

The pentafluorophenyl derivatives $(C_6F_5)_3Ti.3THF$ and $(C_6F_5)_3V.THF$ have been synthesised by the reaction of $MCl_3.3THF$ with C_6F_5MgBr or C_6F_5Li. The authors of the present review established that the reaction conditions play a major role in the successful isolation of the compounds: the use of THF as the solvent, the optimum temperature range from 0° to +5 °C, and the order in which the reactants are added (it is essential that transition metal halide be added to the Grignard reagent)[21,48].

2. The Synthesis of Alkyl(aryl) Metal Halides

The main method of synthesis of organometallic halides involves the interaction of transition metal halides with alkylating (arylating) agents using different ratios of the initial reactants. The importance of the synthesis of compounds of the type R_nMHal_{m-n} is due to the possibility of their being used for the synthesis of other classes of substances.

The Benzyl Derivatives (Table 4)

The possibility of obtaining benzylmetal halides by the double decomposition reaction between MCl_4 and $PhCH_2MgCl$ has been investigated in relation to titanium. The reaction of $TiCl_4$ with different amounts of $PhCH_2MgCl$ in Et_2O at −20 °C leads to the reduction of titanium and the formation of bibenzyl[49]. Other methods of synthesis of benzyl titanium and benzylzirconium halides have therefore been used. A novel electrochemical method of synthesis of complexes of dibenzylmetal dihalides with bipyridyl or acetonitrile, having the general formula $(PhCH_2)_2MHal_2.L$ (M = Ti, Zr, or Hf; Hal = Cl, Br, or I; L = bipy or 2MeCN), has been proposed recently[51]. It consists in the chemical oxidation of the titanium subgroup metals in an electrolytic cell containing $PhCH_2Hal$ and acetonitrile or α,α-bipyridyl. The reactions are carried out in solution at a constant current of 30 mA (25 V). The process terminates with the precipitation of the insoluble complexes indicated above.

Benzylvanadium(IV) halides and benzylniobium(V, IV) have not been isolated in a pure state, since they decompose in the reaction solution at the instant of formation[7,52]. It proved possible to isolate certain benzyltantalum halides as a result of double decomposition reactions[10 12].

Particular attention has been devoted to the problem of the synthesis and investigation of the reactivities of benzyltitanium(III) halides, because it is believed that such titanium(III) derivatives enter into the decomposition of the active centres in various catalytic systems based on organotitanium compounds. In connection with the synthesis of $(PhCH_2)_n.TiHal_{3-n}$, a method for the substitution of the benzyl group in $(PhCH_2)_3Ti$ by a halogen involving treatment with HCl or I_2 was employed. The reaction of $(PhCH_2)_3Ti$ with gaseous HCl (in proportions of 1 : 1 and 1 : 2) was carried out in o-xylene at −20 °C. The reaction of $(PhCH_2)_3Ti$ with I_2 in toluene at −20 °C yields products with various degrees of alkylation depending on the initial reactant ratio[19]. It has been established that benzyltitanium(III) halides undergo quantitatively the oxidative-reductive disproportionation reaction on raising the temperature to 20 °C. However, the composition of the disproportionation products changes on passing from the chlorides to the iodides:

$$2\,(PhCH_2)_2\,TiCl \rightarrow TiCl_2 + (PhCH_2)_4\,Ti\,,$$
$$2\,(PhCH_2)_2\,TiI \rightarrow PhCH_2TiI + (PhCH_2)_3\,TiI\,.$$

The Trimethylsilylmethyl and Neopentyl Derivatives (Table 5)

The double decomposition reaction between $TiCl_4$ and Me_3SiCH_2MgCl or Me_3SiCH_2Li was used to synthesise $(Me_3SiCH_2)_nTiCl_{4-n}$ ($n = 1, 2, 3$); depending on the initial reactant ratio, it led to the isolation of $Me_3SiCH_2TiCl_3$ and $(Me_3SiCH_2)_2TiCl_2$.[53] The attempts at the synthesis of

Table 5. Neopentyl- and trimethylsilylmethyl-metal halides R_nMCl_{m-n} (R = CH_2CMe; R' = CH_2SiMe_3; n = 1, 2, 3, 4; m = 4, 5).

Alkylmetal halide	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MCl_n	R_nE, R'_nE	solvent	t, °C		colour	m.p., °C	
$R_2'TiCl_2$	$TiCl_4$	R'Li	hexane	—3	14	red-brown	—(65/1.5 mm)[a]	[53]
$R'TiCl_3$	$TiCl_4$	R'MgCl	hexane + Et_2O	—20	40	red-orange	—(45/1.5 mm)[a]	[53]
$R_2ZrCl_2 \cdot PMe_3$	$ZrCl_4$	RLi	Et_2O+PMe_3	20	90	yellow	50[b]	[54]
$[(Me_3Si)_2CH]_3ZrCl$	$ZrCl_4$	$(Me_3Si)_2CHLi$	Et_2O	20	45	colourless	–[c]	[32]
$[(Me_3Si)_2CH]_3HfCl$	$HfCl_4$	$(Me_3Si)_2CHLi$	Et_2O	20	53	colourless	–[c]	[32]
R_4TaCl	$TaCl_5$	RLi	pentane	—78	—[d]	yellow	25[d]	[28]
R_3TaCl_2	$TaCl_5$	R_2Zn	pentane	20	85	yellow	—(110/1 mm)[f]	[28]
R_2TaCl_3	$TaCl_5$	R_2Zn	toluene	20	d	yellow	25[d]	[28]
$RTaCl_4$	$TaCl_5$	R_2Zn	toluene	20	92	yellow	25[d]	[56]
$R_3'TaCl_2$	$TaCl_5$	$R_2'Zn$	Et_2O	0	77[d]	yellow	68	[55]
$R_2'TaCl_3$	$TaCl_5$	$R_2'Zn$	Et_2O	10	74	yellow	70	[55]
$R'TaCl_4$	$TaCl_5$	R'_2Zn	Et_2O	20	65	yellow	59	[55]
R_3NbCl_2	$NbCl_5$	R_2Mg	Et_2O	20	35	orange	70[d]	[28]
R_2NbCl_3	$NbCl_5$	R_2Zn	pentane	20	80	red-orange	25[d]	[57]
$R_3'NbCl_2$	$NbCl_5$	$R_2'Zn$	Et_2O	—10	53	orange-red	70	[55]

Remarks: [a]liquid, b.p. is indicated; [b]decomposes in benzene; [c]m.p. not determined; [d]yield not indicated; [e]melts with decomposition; [f]sublimation temperature.

Table 6. Mesityl- and pentafluorophenyl-metal halides R_nMCl_{m-n} (R = Mes; R' = C_6F_5; n = 1, 2, 3; m = 4, 5).

Arylmetal halide	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MCl_n	R_nE, R'_nE	solvent	t, °C		colour	m.p., °C	
$RTiCl_3$	$TiCl_4$	R_2Zn	pentane	20	56	red-orange	82	[61]
$RTiBr_3$	$TiBr_4$	R_2Zn	pentane	20	74	red	62	[61]
R_3NbCl_2	R_2NbCl_3	RLi	toluene	20	10	orange	—[a]	[62]
R_2NbCl_3	$NbCl_5$	R_2Zn	toluene	20	84	red	—[a]	[62]
$RNbCl_4$	$NbCl_5$	R_2Zn	pentane	20	85	dark-red	25[b]	[62]
R_3TaCl_2	R_2TaCl_3	RLi	toluene	20	71	yellow	—[a]	[62]
R_2TaCl_3	$TaCl_5$	R_2Zn	toluene	20	74	orange	—[a]	[62]
$RTaCl_4$	$TaCl_5$	R_2Zn	pentane	20	93	orange-red	25[c]	[62]
$RVCl_2 \cdot 2THF$	$VCl_3 \cdot 3THF$	RMgBr	THF	—30	36	brown-yellow	91[b]	[65]
$R_3'VCl \cdot THF$	VCl_4	R'Li	hexane	—70	70	red-violet	200[b]	[63]
$R_2'VCl_2 \cdot THF$	VCl_4	$R_2'V$	THF	—70	57	red	220[b]	[63]
$R'VCl_3 \cdot THF$	VCl_4	$R_2'V$	THF	—70	54	raspberry red	125	[63]

Remarks: [a]m.p. not determined; [b]decomposes without melting; [c]stable at 25 °C.

$(Me_3SiCH_2)_3.TiCl$ were unsuccessful, since this compound readily disproportionates in solutions[53]:

$$2\,(Me_3SiCH_2)_3\,TiCl \xrightarrow[20^\circ C]{\text{hydrocarbons}} (Me_3SiCH_2)_4\,Ti + (Me_3SiCH_2)_2\,TiCl_2\ .$$

Trialkylmetal halides which do not undergo disproportionation have been synthesised using the $(Me_3Si)_2CH$ bulky substituent. The double decomposition reaction of MCl_4 even with an excess $[(Me_3Si)_2CH]Li$ always leads to the isolation of $[(Me_3Si)_2CH]_3MCl$ (M = Zr or Hf). When attempts were made to obtain the analogous titanium compound, reduction with formation of $[(Me_3Si)_2CH]_3Ti$ was observed[32]. Neopentylzirconium chlorides have been obtained recently[54]: the reaction of $ZrCl_4$ with two moles of Me_3CCH_2Li in Et_2O yields $(Me_3CCH_2)_2ZrCl_2.Et_2O$ in the form of an oil, while crystalline products are isolated on formation of complexes with phosphines and amines. Procedures whereby the symmetrical $(Me_3CCH_2)_2ZrCl_2$ is converted into mono- or tri-neopentylzirconium chloride are being investigated[54].

It has been shown that trimethylsilylmethylvanadium(IV) halides as well as $(PhCH_2)_nVCl_{4-n}$ are unstable in solution and decompose with formation of low-valence vanadium complexes[21].

Organozinc compounds can be used successfully to isolate a whole series of derivatives of the type $(Me_3ECH_2)_nMCl_{5-n}$ (M = Nb or Ta; E = C or Si; n = 1, 2, 3, 4). With the aid of organozinc compounds, it is possible to substitute in succession the chlorine atoms in MCl_5 for the Me_3ECH_2 groups[28,55–57]. For the Group IVB metals, only the molybdenum complex $(Me_3SiCH_2)_3MoCl.PMe_3$ has been isolated[58].

The methods of synthesis of the compounds $(Me_3SiCH_2)_n.TiCl_{3-n}$ have been investigated by analogy with $(PhCH_2)_n.TiCl_{3-n}$. It has been established that they exist in solutions at temperature not exceeding –5 °C. When attempts were made to isolate them, oxidative-reductive disproportionation to the titanium(II) and Ti(IV) complexes was always observed[59,60].

The Mesityl Derivatives (Table 6)

Attempts to obtain mesitylmetal halides have now been described for titanium(IV), niobium(V), tantalum(V), and vanadium(III). Mes_2Zn is the best arylating agent. The reaction of $TiCl_4$ with Mes_2Zn in proportions of 2 : 1 yields $MesTiCl_3$.[61]

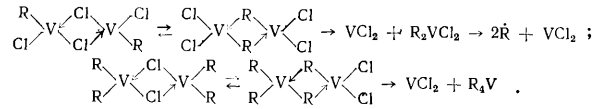
Depending on the initial reactant ratio, it is possible, as for the Me_3ECH_2 substituents, to replace in succession the chlorine atoms by the Mes groups by the reaction of MCl_5 (M = Mb or Ta) with Mes_2Zn. $MesMCl_4$ and Mes_2MCl_3 have been obtained in this way[62]. The substitution of the third chlorine atom by the mesityl group is possible when MesLi is used. It has been established that the thermal stability of mesitylmetal chlorides diminishes with increase of the degree of arylation. Thus $MesTaCl_4$ sublimes without signs of decomposition, $MesNbCl_4$ decomposes in the solid state at 25 °C after several days, while Mes_2NbCl_3 decomposes faster than the monosubstituted product under these conditions: Mes_3TaCl_2 and Mes_3NbCl_2 always contain decomposition products[62].

The Pentafluorophenyl Derivatives (Table 6)

Compared with other compounds, the σ-C_6F_5-substituted derivatives have been investigated to only a fairly slight extent. A series of pentafluorophenylmetal chlorides have now been investigated for Group VB metals[63].

The reactions of MCl_5 (M = Nb or Ta) with C_6F_5Li in various proportions (ranging from 1 : 3 to 1 : 6) in hexane at −78 °C give rise to solid variable-composition products $(C_6F_5)_nMCl_{5-n}$, where n = 2, 3; the molecular weight is intermediate between those of the monomer and the dimer[64].

A detailed study has been made in order to synthesise alkylvanadium(III) chlorides R_nVCl_{3-n} (n = 1, 2) with substituents of different kinds (R = CH_2Ph, CH_2SiMe_3, Mes, or C_6F_5). For this purpose, the double decomposition reaction of VCl_3.3THF with RMgCl in proportions of 1 : 1 and 1 : 2 in Et_2O or THF as well as the reactions of R_3V.THF (R = CH_2. .$SiMe_3$ or C_6H_5) with gaseous HCl were investigated[21]. The attempts to isolate $RVCl_2$ and R_2VCl were unsuccessful. It has been established that the above derivatives undergo oxidative-reductive disproportionation in solutions at 0 °C. This process proceeds via a stage involving the formation of intermediate dinuclear complexes in which chlorine atoms are exchanged for the ligands R. The composition of the disproportionation products is determined by the ratio of the amounts of R and Cl in the initial reactant R_nVCl_{3-n}:



Evidently when a bulky ligand with structural rigidity is used, there is a possibility, on the one hand, that the monomeric form is stabilised and, on the other hand, that the exchange of a chlorine atom for a ligand R in the dinuclear complex, which subsequently decomposes, may be hindered. Such requirements are met by the mesityl ligand. Indeed the double decomposition reaction of VCl_3.3THF with MesMgBr in THF at a low temperature led to the isolation of the pure compound $MesVCl_2$.2THF, which is entirely stable on heating to 100 °C.[65]

3. The Synthesis of the Compounds R_nMX_{m-n} (X = OR', acad, or NR'_2; m = 3, 4, 5; n = 1, 2, 3)

The thermal stability of compounds of this type is determined not only by the characteristics of the σ-substituents considered in this review but also by the properties of the group X. The alkoxy-derivatives are thermally stable by virtue of the formation of dimers, since the R'O groups tend to associate. The acetylacetonate group reacts with the metal to form an intramolecular chelate. The R'_2N group promotes the coordination and saturation of the metal in the molecule. Furthermore, an increase of thermal stability is observed when bulky amide groups are used. The specific features of the above OR', NR'_2, and acac groups are responsible for the isolation of individual compounds containing methyl, ethyl, and phenyl groups (Tables 7 and 8).

The compounds $RTi(OPr\text{-}iso)_3$ (R = Me, Ph, or C_6H_5) and $R_2Ti(OEt)_2$ (R = CH_2Ph, or C_6H_{11}) have been obtained; they exist in the form of dimers[5,66,67,68].

The diphenoxides are monomeric and their thermal stability is determined to a large extent by the nature of the σ-substituent. The derivatives $(Me_3SiCH_2)_2Ti(OPh)_2$ is stable up to 100 °C, while the analogous dimethyl compound decomposes rapidly in solution at 20 °C.[69]

Studies of the synthesis of $(PhCH_2)_3TiOEt$, $RV(OR')_3$, and R_3VOR' have shown that they are readily symmetrised[5,70]. The compounds $R_2V(OR')_2$, which have been obtained in three different ways, proved to be thermally stable[70,71] (Table 7).

Table 7. Alkoxy-derivatives $R_nM(OR')_{4-n}$ and acetylacetonates $R_nM(acac)_{m-n}$.

Derivative	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MX_n	reagent	solvent	t, °C		colour	decomp. temp., °C	
$(PhCH_2)_2Ti(OEt)_2$	$(PhCH_2)_4Ti$	EtOH	benzene	+5	70	red-orange	110	[5]
$(Me_3SiCH_2)_2Ti(OPh)_2$	$Cl_2Ti(OPh)_2$	R_2Mg	Et_2O	−70	20	yellow	100	[69]
$C_6F_5Ti(OPr\text{-}iso)_3$	$ClTi(OPr\text{-}iso)_3$	C_6F_5Li	Et_2O	−70	17	colourless	135	[67]
$(PhCH_2)_2V(OBu\text{-}t)_2$	$(PhCH_2)_4V$	t-BuOH	hexane	−10	43	green	152	[70]
$(Me_3SiCH_2)_2V(OBu\text{-}t)_2$	$Cl_2V(OBu\text{-}t)_2$	RMgCl	Et_2O	−70	20	blue-green	148	[71]
$Mes_2V(OBu\text{-}t)_2$	$V(OBu\text{-}t)_4$	RMgBr	Et_2O	−70	80	green	176	[71]
$(C_6F_5)_2V(OBu\text{-}t)_2$	$(C_6F_5)_4V$	t-BuOH	Et_2O	−70	87	dark green	179	[71]
$(PhCH_2)_2Zr(acac)_2$	$(PhCH_2)_4Zr$	(acac)H	Et_2O	−40	71	yellow	125	[72]
$(PhCH_2)V(acac)_2$.THF	$V(acac)_3$	RMgCl	THF	−50	80	red-brown	100	[73]
$(Me_3SiCH_2)V(acac)_2$.THF	$V(acac)_3$	RMgCl	THF	−50	80	red-brown	112	[73]
$(C_6F_5)V(acac)_2$.THF	$V(acac)_3$	RMgBr	THF	−50	80	red-brown	128	[73]
$(PhCH_2)Cr(acac)_2$	$Cr(acac)_3$	RMgCl	Et_2O	−70	15	yellow-green	0	[17]

Table 8. Amido-derivatives $R_nM(NR''_2)_{4-n}$ and $R'_nM(NR''_2)_{4-n}$ ($R = CH_2Ph$, $R' = CH_2SiMe_3$).

Derivative	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MX_n	reagent	solvent	t, °C		colour	m.p., °C	
R_3TiNEt_2	Br_3TiNEt_2	RMgCl	Et_2O	—20	87	red	10[a]	[75]
$R_2Ti(NEt_2)_2$	$Br_2Ti(NEt_2)_2$	RMgCl	Et_2O	—20	38	red	—10[b]	[75]
$RTi(NEt_2)_3$	$BrTi(NEt_2)_3$	RMgCl	Et_2O	—20	78	red-orange	13	[75]
R_2TiPip_2	Br_2TiPip_2	RMgCl	Et_2O	—20	87	red	20[a]	[75]
$R_2Ti(CTS)_2$	$Br_2Ti(CTS)_2$	RMgCl	PE	—10	68	red	131	[76]
$R'_2Ti(NEt_2)_2$	$Br_2Ti(NEt_2)_2$	R'MgCl	Et_2O	—20	84	yellow-orange	0[b]	[75]
$R'Ti(NEt_2)_3$	$BrTi(NEt_2)_3$	R'MgCl	Et_2O	—20	91	yellow	0[a]	[75]
$R_2Zr(NPh_2)_2$	R_4Zr	Ph_2NH	benzene	+20	50	yellow	—[c]	[80]
$R'_2Hf[N(SiMe_3)_2]_2$	$Cl_2Hf[N(SiMe_3)_2]_2$	R'MgCl	Et_2O	0	89	colourless	91	[78]
Mes_3VNPh_2	$[Mes_3VNPh_2]Li$	O_2	—	+20	84	black	124	[81]

Remarks: [a]melts with decomposition; [b]decomposes in solution; [c]m.p. not determined. Pip = piperidine; CTS = octamethyl-2,4,6-trisila-1,3,5-triazacyclo-hex-1-yl.

The acetylacetonate derivatives have been investigated in relation to the zirconium and vanadium compounds (Table 7). While $(PhCH_2)_2Zr(acac)_2$ is fairly stable, $R_2V(acac)_2$ and also $RV(acac)_3$ undergo reductive elimination in solutions[72,73]. The derivatives $(Me_3SiCH_2)_3Zr(acac)$ and $R_3V(acac)$ are readily symmetrised. Systematic studies have been made of the synthesis and properties of mixed σ-derivatives of vanadium of the type R_nVX_{m-n} ($R = CH_2Ph$, CH_2SiMe_3, or C_6H_5; X = Cl, OBu-t, or acac; $n = 1, 2, 3$; $m = 3, 4$). It has been established that, regardless of the nature of the σ-substituent, the compounds RVX_3, RVX_2, and R_2VX_2 (X = Cl or acac) undergo reductive decomposition in Et_2O.[21] $RTi(OBu\text{-}t)_3$ and $R_2V(OBu\text{-}t)_2$ are exceptions owing to the large bulk and low electronegativity of the t-butoxy-groups. The derivatives RVX_3 are symmetrised, while the RVX_2 undergo oxidative-reductive disproportionation in solutions (regardless of the nature of X and R), which proceeds via a stage involving the formation of intermediate dinuclear complexes.

When the reaction mixture contains agents preventing the formation of dinuclear complexes and stabilising the monomeric form, stable products are isolated, for example, the compounds $RV(acac)_2.THF$, stabilised by the formation of the monomeric hexacoordinate complex, since the acetylacetonate group is a η^2-ligand.

Studies of a series of alkylamide derivatives of titanium established that the thermal stability of the compounds decreases in the sequence $RTi(NR'_2)_3 > R_3TiNR'_2 > R_2Ti(NR'_2)_2$. It was found that, in contrast to R_2TiX_2 (X = Hal or OR), the compounds $R_2Ti(NR'_2)_2$ readily disproportionate[74,75]:

$$3R_2Ti(NR'_2)_2 \xrightarrow[-20°C]{} 2RTi(NR'_2)_3 + R_4Ti \ .$$

The stabilisation of the symmetrical compounds has been achieved by employing rigidly fixed or bulky ligands (Table 8). X-Ray diffraction analysis of $MeHf[N(SiMe_3)_2]_3$ has shown that the $(Me_3Si)_2N$ groups are located in space in such a way that they fully shield the central atom from external influences[77]. By virtue of this spatial disposition of the $(Me_3Si)_2N$ groups, even the compound $Et_2Hf[N(SiMe_3)_2]_2$ (m.p. 65 °C) is thermally stable, although the ethyl derivatives of transition metals usually exist only at low temperatures because of the ease of β-elimination[78,79].

The amide derivatives of vanadium(IV) and vanadium(III) have been scarcely investigated. A single compound $Mes_3.VNPh_2$ has been synthesised by oxidising the corresponding ate-complex $[Mes_3VNPh_2]^-Li^+$.[81] The isolation of $MesV(NPh_2)_2$, formed by the reaction

$$VCl_3 \cdot 3THF + MesMgBr + 2KNPh_2 \rightarrow MesV(NPh_2)_2 \ ,$$

has been mentioned. No detailed description of the reaction conditions and the properties of the compounds is given[82].

III. THERMAL DECOMPOSITION OF THE σ-DERIVATIVES

The task of the study of the thermal decomposition of the individual σ-derivatives R_nM and R_nMX_{m-n} is the determination of the general features of this process as a function of the electronic configuration, coordination capacity of the central atom, and the decomposition conditions.

An attempt has been made at a theoretical justification of the modes of decomposition by analysing the correlation between the symmetry groups of the valence orbitals of the metal atoms in the initial σ-complex and its thermolysis products. On the basis of these correlations, the metal complexes with the electronic configurations $d - d^8$ should undergo reductive elimination. For the complexes with the electronic configurations d^0[Ti(IV), Zr(IV), and Hf(IV)] and d^1, d^2[V(IV), Cr(IV), Ti(III), and V(III)], the reductive elimination is prohibited and the σ-bond is homolysed[83]. The experimental results obtained by different workers are in good agreement with these theoretical postulates.

It has been established that reductive elimination is observed on thermolysis of the neophyl complexes of chromium(III) (d^3 system), Mn(II), Fe(III) (d^5 system), Fe(II), Co(III) (d^6 system), Co(II) (d^7 system), and Ni(II) (d^8 system) and leads to the formation of bineophyl and to a decrease of the valence of the central atom[84].

The elimination processes are varied. Apart from the reductive elimination, the complexes are decomposed via α-, β-, and γ-hydride elimination.

The classical compounds which decompose via α-elimination are the σ-derivatives of niobium and tantalum. The study of the kinetics of the thermal decomposition of $(PhCH_2)_5Ta$ in benzene at 40 °C in the presence of an initiator (azobisisobutyronitrile) or an inhibitor (the galvinoxy-radical) has shown that the decomposition of $(PhCH_2)_5Ta$ does not entail the homolysis of the M—C bond with formation of free radicals[85]. The authors believe that $(PhCH_2)_5Ta$ decomposes via intramolecular or intermolecular α-hydride elimination with formation of toluene and alkylidene complexes of quinquevalent tantalum. However, the individual compound could not be isolated in this instance. The neopentylidene complex $(Me_3CCH_2)_3Ta(CHCMe_3)$ proved to be thermally stable[28]. The analogous niobium complex is unstable. The authors[28] postulate the formation of the tantalum complex via the decomposition of the short-lived $(Me_3CCH_2)_5Ta$, whose molecules have a trigonal bipyramidal structure. Its relatively more acidic α-proton passes from the α-carbon atom of the equatorial alkyl group to the relatively more nucleophilic α-carbon atom of the axial alkyl group. This results in a rearrangement of the structure accompanied by the formation of Me_4C and the

final pseudotetrahedral complex. Schrock's investigations[12, 28,85] suggest that the decomposition of all the pentacoordinate niobium(V) and tantalum(V) complexes takes place via α-elimination with formation of tetracoordinate alkylidene complexes of formally quinquevalent niobium and tantalum[28].

The α-elimination process is dominant in the decomposition of alkylmolybdenum and alkyltungsten halides R_nMHal_{m-n} ($R = CH_2Ph$ or CH_2SiMe_3). The factor favouring this reaction pathway is the possibility of the stabilisation of carbenes on coordination to molybdenum and tungsten. The main evidence confirming the elimination of α-hydrogen is as follows: firstly, the Me_4Si formed on decomposition of $(Me_3.SiCH_2)_nMHal_{m-n}$ in deuterated solvents does not contain deuterium atoms and, secondly, the decomposition of the dry residues (after the decomposition of the compound) with heavy water results in the formation of considerable amounts of Me_3SiCHD_2 and $PhCHD_2$.[86-88]

Thus, in the decomposition of $Mes(Me)TaCl_3.PMe_3$ in toluene at 45 °C or of $Mes(Me)TaBr_3.PMe_3$ in $CHCl_3$ at 25 °C, the Me–Ta bond is cleaved homolytically and CH_4 is formed as a result of the abstraction of the γ-hydrogen from the Mes group. ^1H and ^{13}C NMR data made it possible to establish the formation of substituted benzylidene complexes and to put forward a γ-elimination mechanism[62]:

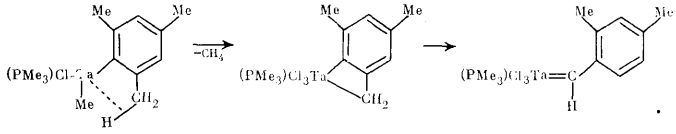


Table 9. Thermolysis of the benzyl and trimethylsilylmethyl derivatives of titanium, zirconium, and vanadium.

Compound	Decomposition conditions (*t*, °C)	Amount of RH, mol/mol OMC	Refs
$(PhCH_2)_4Ti$	solid (100)	2.2	[89, 90]
$(PhCH_2)_4Ti$	in heptane (100)	2.5	[5]
$(PhCH_2)_4Zr$	solid (135)	2.5	[90]
$(PhCH_2)_4Zr$	in octane (100)	2.5	[5]
$(PhCH_2)_4Zr$	in toluene (100)	2.5	[5]
$(PhCH_2)_4V\cdot 2Et_2O$	solid[a] (80)	2.4	[91]
$(PhCH_2)_4V\cdot 2Et_2O$	in benzene (80)	3.8	[91]
$(PhCH_2)_4V\cdot 2Et_2O$	in ether (80)	3.8	[91]
$(PhCH_2)_3V\cdot THF$	in THF (0)	2.8	[91]
$(Me_3SiCH_2)_4V$	solid (95)	2.8	[91]
$(Me_3SiCH_2)_4V$	in benzene (90)	2.8	[91]
$(Me_3SiCH_2)_4V$	in THF (90)	2.8	[91]
$(Me_3SiCH_2)_3V\cdot THF$	solid[a] (75)	1.9	[91]
$(Me_3SiCH_2)_3V\cdot THF$	in hexane (75)	2.0	[91]
$(Me_3SiCH_2)_3V\cdot THF$	in ether (75)	2.0	[91]

Remarks: [a] the decomposition was carried out in a quasi-flow system permitting the removal of the eliminated ligand from the reaction zone.

It is nowadays regarded as generally accepted that the decomposition of the σ-derivatives of Ti, Zr, Hf, V, Cr, Mo, and W is accompanied by the homolysis of the σ-bond. The thermolysis of the benzyl derivatives $(PhCH_2)_4M$ (M = Ti, Zr, Hf, V, Mo, or W) in the solid state and in solutions entails the formation of mainly toluene. At the same time very small amounts of bibenzyl, benzene, diphenylmethane, methane, and ethane were detected. The metal-containing thermal decomposition products consist of dark involatile pyrophoric substances in which the metal is present in a low-valence state. Unfortunately quantitative data have been obtained only for titanium, zirconium, and vanadium[5,89,90,91] (Table 9).

The trimethylsilylmethyl and neopentyl compounds of the elements in the titanium and vanadium subgroups decompose to give Me_4E (E = C or Si) as the only volatile product. No detailed studies of the thermolysis of $(Me_3ECH_2)_4M$ (M = Ti, Zr, Hf) have so far been made. It has been established that the thermolysis of the trimethylsilylmethyl derivatives of vanadium(IV) and vanadium(III) under various conditions leads to the formation of black pyrophoric residues containing low-valence vanadium[91].

There are virtually no quantitative literature data on the thermolysis of mesityl derivatives. The high thermal stability of the compounds Mes_4M (M = Ti, V, Cr, or Mo), which decompose above 100 °C, has been noted[34-37]. The decomposition results in the formation of mainly mesitylene together with small amounts of xylene, toluene, and bimesityl. For example, in the decomposition of the Mes_4Ti the product ratios are $MesH : Me_2C_6H_4 : MeC_6H_5 : Mes_2 = 100 : 0.1 : 10 : 4.7$.[92] The decomposition of $Mes_3V.THF$ is accompanied by the elimination of THF followed by the splitting off of more than 90% of the σ-substituents. The decomposition products are mesitylene, xylene, toluene, and bimesityl in the proportions 100 : 6.3 : 2.3 : 6.3.[93]

Thus the first stage of the thermolysis is the homolysis of the R–M σ-bond regardless of the valence of the central atom. If the compound has a coordinated ligand, its decomposition usually begins with the elimination of the ligand molecule. It has been established by physicochemical methods that the eliminated σ-substituents do not become free radicals. Consequently their subsequent reactions take place intramolecularly or intermolecularly within a cage. The reaction products of the homolytic species are RH. The sources of hydrogen can be (1) the groups R bound to the metal, (2) the ligand coordinated to the central atom, and (3) the solvent molecules.

It has been established that Me_4Si is formed in the decomposition of the Me_3SiCH_2 derivatives only via the intramolecular or intermolecular elimination of the hydrogen atom from the groups R bound to the central atom. Neither the coordinated ligands nor solvent molecules serve as sources of hydrogen. After the elimination of THF in the first stage of the thermolysis of $(Me_3SiCH_2)_3V.THF$, a structural rearrangement takes place with formation of the dimer $[(Me_3SiCH_2)_6V_2]$. The large bulk of the Me_3SiCH_2 groups and the small radius of the vanadium atom hinder its coordination to THF or Et_2O in the dimer and also in $(Me_3SiCH_2)_4V$.[91,94]

The benzyl derivatives decompose in the solid state via the same mechanism as the Me_3SiCH_2 derivatives but in solutions a difference is observed. Since the $PhCH_2$ groups are less bulky than the Me_3SiCH_2 ligands, they do not hinder the coordination of the THF or Et_2O to vanadium. Although the thermolysis of the complexes $(PhCH_2)_4V.2Et_2O$ and $(PhCh_2)_3V.THF$ begins with the loss of the coordinated ligand, a mobile equilibrium exists in solutions:

$$(PhCH_2)_nV\cdot xL \rightleftharpoons (PhCH_2)_nV + xL \quad ;$$

$$n = 3, 4;\ L = Et_2O,\ THF;\ x = 1, 2 \quad .$$

The occurrence of the reversible reaction makes it possible to replace the ligand by a molecule of the solvent capable of coordination, which serves in its turn as a hydrogen donor. Consequently in the decomposition reaction in solutions, the sources of hydrogen for the formation of RH can be both the groups R bound to the metal and the molecules of the coordinated ligand. The occurrence of two pathways is confirmed by the quantitative yield of toluene and by the analysis of the solid residue. In the decomposition of organovanadium

Table 10. $(C_6F_5)_nM.xL$ decomposition products[48,91,95].

Compound	decomp. temp., °C	Decomposition conditions		Decomposition products, mol/mol R_nM				
		solvent	t, °C	C_6F_5H	$(C_6F_5)_2$	$C_6F_4-C_6F_6$	$(C_6F_4)_3$	MX_n
$(C_6F_5)_4Ti\cdot2Et_2O$	130	THF	90	0.20	—	—	1.02	TiF_4+TiF_3
$(C_6F_5)_4Ti\cdot2Et_2O$	130	benzene	100	0.20	0.10	2.80	—	TiF_4+TiF_3
$(C_6F_5)_3Ti\cdot3THF$	122	solid[a]	130	—	—	—	0.81	TiF_3
$(C_6F_5)_3Ti\cdot3THF$	122	THF	90	0.83	—	—	0.63	F_2TiOR
$(C_6F_5)_3Ti\cdot3THF$	122	benzene	90	0.70	—	1.83	—	F_2TiOR
$(C_6F_5)_4V\cdot2THF$	205	Et_2O	90	0.70	0.10	—	—	$(C_6F_5)_3V.THF$
$(C_6F_5)_4V\cdot2THF$	205	Bu_2O	140	0.65	0.10	—	1.03	$VF_3.THF$
$(C_6F_5)_4V\cdot2THF$	205	benzene	140	0.77	0.10	2.83	—	$VF_3.THF$
$(C_6F_5)_3V\cdot THF$	220	Bu_2O	140	—	—	—	0.96	$VF_3.THF$
$(C_6F_5)_3V\cdot THF$	220	benzene	140	—	—	2.93	—	$VF_3.THF$

Remarks: [a] decomposition in a quasi-flow system; amount of THF 2.75 mol/mol $(C_6F_5)_3Ti.3THF$. A dash indicates that the given compound was not detected in the decomposition products.

compounds the solid residue contains the V–OR fragments which have arisen from secondary oxygen-containing ether groups. The study of the thermal decomposition of $(PhCH_2)_4V.2Et_2O$ in di-isopropyl ether by EPR revealed the formation of the intermediate derivative $(PhCH_2)_2V(OPr\text{-}iso)_2$.

The solvent is not involved in the formation of RH in the thermolysis of the benzyl derivatives of titanium and zirconium in hydrocarbons. This is confirmed by data for the decomposition of $(PhCH_2)_4Zr$ in $C_6D_5CD_3$, which does not result in the formation of $PhCH_2D$. The thermolysis of the equimolar $(PhCH_2)_4Ti + (C_6D_5CD_2)_4Ti$ mixture in heptane leads to the formation of toluene deuterated to different extents. This indicates the existence of an intermolecular pathway leading to the elimination of hydrogen. Unfortunately the decomposition of $(PhCH_2)_4M$ (M = Ti or Zr) in solvents capable of coordination (Et_2O, THF) has not been studied in detail and it is therefore difficult to reach a general conclusion concerning the influence of the nature of the solvent on the RH formation pathways.

The influence of the nature of the σ-substituent and of solvent character is clearly manifested in the thermolysis of the pentafluorophenyl derivatives of titanium and vanadium[48, 91,95] (Table 10). The titanium compounds decompose without fusion in the temperature range 120–130 °C, while the vanadium compounds decompose at 205–220 °C. The thermograms of the titanium complexes show that the coordinated ligands are split off initially. In contrast to this, the thermograms of the vanadium complexes have no peaks corresponding to the elimination of THF. The difference between the first stages of the decomposition determines also the difference between the subsequent decomposition pathways.

In compounds with the C_6F_5 ligands there is a possibility of the interaction of the unshared electron pair of the fluorine atom in the *ortho*-position with the *d* orbital of the metal. In the complexes $(C_6F_5)_4Ti.2Et_2O$, $(C_6F_5)_3Ti.3THF$, and $(C_6F_5)_4V.2THF$, the central atom is coordination-saturated and there is therefore initially no additional coordination of the fluorine to the metal. Experimental data show that the coordinated Et_2O or THF ligands are split off initially in the decomposition of the titanium derivative and one of the C_6F_5 groups is the first to be split off in the case of vanadium. This is probably followed by a rearrangement of the coordination sphere of the central atom associated with the fact that the vacant sites in the octahedral configuration are occupied by fluorine atoms. This additional coordination weakens both the $C-F_{ortho}$ and the C–M bonds. Both bonds are therefore ruptured in the thermolysis, which is accompanied by a transfer of the fluorine to the metal atom and the formation of metal fluorides. The fluorinated ligand is split off in the form of tetrafluorodehydrobenzene and the subsequent reaction pathways of C_6F_4 depend only on the nature of the solvent. C_6F_4 does not react with ethers and trimerises, but it does enter into a reaction with benzene of the type of diene synthesis with formation of 5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene.

The C_6F_5 groups eliminated from vanadium in the thermolysis of $(C_6F_5)_4V.2THF$ are converted mainly into C_6F_5H as a result of the abstraction of hydrogen from the coordinated THF molecules. A small proportion of the C_6F_5 groups dimerise. The formation of small amounts of C_6F_5H in the decomposition of $(C_6F_5)_4Ti.2Et_2O$ shows that the loss of coordinated ligands is accompanied by the partial homolysis of the C_6F_5–Ti σ-bond. On thermal decomposition in solutions, the compound $(C_6F_5)_3Ti.3THF$ remains coordination-saturated and for this reason one observes under the given conditions in the first stage the elimination of the C_6F_5 group, which is converted into C_6F_5H as a result of the abstraction of hydrogen from THF. Owing to the octahedral configuration, two vacant sites are produced and are occupied by the fluorine atoms from the two remaining C_6F_5 groups. The subsequent decomposition leads to the elimination of two C_6F_4 groups and the transfer of two fluorine atoms to titanium. However, $F_2Ti(OR)$ is formed instead of TiF_2, since the alkoxy-group produced due to the decomposition of the dehydrogenated THF adds to titanium. In $(C_6H_5)_3V.THF$ there is a possibility of the expansion of the coordination sphere to an octahedron as a result of the coordination of fluorine to vanadium. The C_6F_4 and not C_6F_5 is therefore split off in the decomposition of $(C_6F_5)_3V.THF$ and $VF_3.THF$ is formed.

Thus the mode of the thermal decomposition of the pentafluorophenyl derivatives is determined by the electronic configuration of the central atom and the possibilities for the rearrangement of the coordination sphere in the decomposition process.

Studies of the thermal decomposition of the compounds R_nMX_{m-n} have been published recently[7,63,96]. They are of interest because they make it possible to follow the influence of the second substituent on the reaction pathway. Under comparable conditions, studies have been made of the decomposition of the halogeno-derivatives R_nVCl_{4-n} having substituents of different kinds (Table 11). R_3VCl decomposition products show that symmetrisation takes place initially in accordance with the equation

$$R_3VCl \rightarrow {}^1/_2R_4V + {}^1/_2R_2VCl_2 \ .$$

When R = CH_2Ph or CH_2SiMe_3, the corresponding products R_4V do not decompose under the experimental conditions and

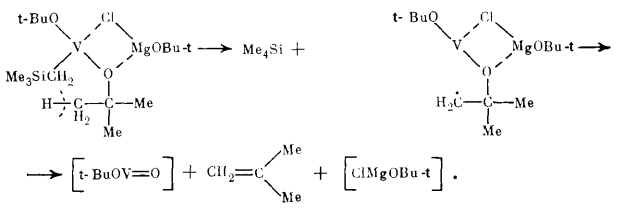
Table 11. R_nVX_{m-n} decomposition products[7,63,96].

Compound	Decomposition conditions		Decomposition products, mol/mol R_nVX_{m-n}		
	solvent	t, °C	RH	R–R	V-containing product (yield)
$PhCH_2VCl_3$	Et_2O	−18	—	0.45	VCl_3 (0.95)
$(PhCH_2)_2VCl_2$	Et_2O	−18	—	0.90	VCl_2 (0.94)
$(PhCH_2)_3VCl$	Et_2O	20	—	0.50	R_4V+VCl_2 (0.40+0.45)
$(Me_3SiCH_2)_3VCl$	Et_2O	20	0.80	—	R_4V+VCl_2 (0.46+0.45)
$C_6F_5VCl_3.THF$	Et_2O	20	0.10	0.45	VCl_3 (0.90)
$(C_6F_5)_2VCl_2.THF$	Et_2O	20	0.40	0.80	VCl_2 (0.90)
$(C_6F_5)_3VCl.THF$[a]	Bu_2O	140	0.67	0.33	VF_3+VCl_2 (0.60+0.33)
$Me_2V(OBu\text{-}t)_2$	Et_2O	90	0.94	—	V(III)+V(II) (0.75+0.15)
$Me_2V(OBu\text{-}t)_2$	heptane	90	0.90	—	V(III)+V(II) (0.75+0.15)
$(PhCH_2)_2V(OBu\text{-}t)_2$	Et_2O	90	0.80	—	V(III)+V(II) (0.75+0.15)
$(PhCH_2)_2V(OBu\text{-}t)_2$	heptane	90	0.70	—	V(III)+V(II) (0.75+0.15)
$Me_3SiCH_2V(OBu\text{-}t)_2.ClMgOBu\text{-}t$	solid[b]	200	0.89	—	V(IV) oxides (0.99)

Remarks: [a] amount of $(C_6F_4)_3$ found 0.60 mol/mol $(C_6F_5)_3VCl.THF$; [b] thermolysis in a quasi-flow system with removal of products from the reaction zone; iso-C_4H_{10} (0.45 mole), iso-C_4H_8 (1.95 mole) and t-BuOH (0.38 mole) were found. A dash indicates that the given compounds was not detected in the decomposition products.

can be isolated from the reaction mixture. The second symmetrisation product (R_2VCl_2) decomposes. The complex $(C_6F_5)_3VCl.THF$ also undergoes symmetrisation initially, but, since it decomposes at 198 °C and $(C_6F_5)_4V.2THF$ decomposes at 205 °C, in the given instance the processes are superimposed and a mixture of decomposition products of both compounds is obtained.

The study of the influence of the t-BuO group on the decomposition of alkylvanadium alkoxides (Table 11) makes it possible to establish that the reaction begins with the homolysis of the V–C σ-bond. At high temperatures (above 200 °C), the V–O and C–O bonds are cleaved. It is noteworthy that $V(OBu\text{-}t)_3$ and $V(OBu\text{-}t)_4$ decompose at 150° and 164 °C respectively. The amounts of RH formed in the decomposition of $R_2V(OBu\text{-}t)_2$ show that the neighbouring R ligands serve as a source of hydrogen. The formation of considerable amounts of CD_4 in the decomposition of $(CD_3)_2V.(OBu\text{-}t)_2$ may serve as confirmation of this finding. The formation of Me_4Si and the subsequent reactions can be represented schematically as follows:



The decomposition temperature determines the composition of the final vanadium-containing products. Below 100 °C, a mixture of alkoxides is produced, while at 200 °C the products consist of a mixture of vanadium oxides.

Regardless of the nature of R and R′, the thermolysis of the compounds $(RCH_2)_nTi(NR'_2)_{4-n}$ (n = 1, 2, 3; R = Ph or $SiMe_3$; R′ = Me or Et) leads to the formation of one mole of RH per RCH_2 group. The titanium remains quadrivalent in all cases[75] (Table 12). An ionic mechanism of the decomposition reaction with participation of the β-hydrogen of the NR_2 groups has been proposed[75]:

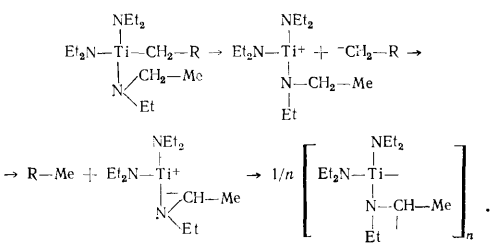


Table 12. Products of the decomposition of $(RCH_2)_n.Ti(NR'_2)_{4-n}$ in the solid state[75].

Compound	Decomp. temp.	RH, moles
$(PhCH_2)_3Ti(NEt_2)$	80	2.2
$(PhCH_2)_2Ti(NEt_2)_2$	80	1.5
$(PhCH_2)Ti(NEt_2)_3$	140	0.8
$(PhCH_2)Ti(NMe_2)_3$	105	0.8
$(Me_3SiCH_2)_2Ti(NEt_2)_2$	90	1.5
$(Me_3SiCH_2)Ti(NMe_2)_3$	90	0.9
$(Me_3SiCH_2)Ti(NEt_2)_3$	130	0.9

Data on the thermolysis of compounds containing bulky amide groups are consistent with the ionic mechanism[76]. The mechanism of the decomposition of the alkylamide compounds is significantly influenced by the presence of the alkylamide group and not by the character of the σ-substituent.

IV. REACTIONS INVOLVING INSERTION IN THE TRANSITION METAL–CARBON σ-BOND

The reactions of the σ-derivatives of transition metals with acids, alcohols, halogens, hydrogen halides, and metal salts have been investigated in fair detail. Numerous investigations established that the above reactions are independent of

the nature of the central atom—the M–C σ-bond is cleaved in all cases. The presence of bulky σ-ligands, such as the adamantyl, norbornyl, and mesityl groups, retards the bond cleavage but the reaction pathway remains unchanged.

An increasing number of studies on the chemistry of organic compounds of transition metals are nowadays devoted to the insertion reactions described by the general formula

$$M-[-R]_n + A \rightarrow M-[-AR]_n .$$

Many such reactions are known, since numerous monatomic and polyatomic species can be inserted in the M–C σ-bond. The reaction pathway is determined, on the one hand, by the nature of the transition metal–carbon σ-bond and, on the other, by the properties of the inserted molecules.

1. Reactions with Oxygen, Sulphur, and Selenium

Virtually all the σ-derivatives of transition metals are sensitive to molecular oxygen. Many compounds undergo spontaneous heating in air. However, if the substance contains bulky substituents, which shield the central atom from coordination with oxygen, it is usually resistant to oxidation. Indeed, Mes_4M and $(adme)_4M$ are not oxidised in air.

Organic compounds of non-transition metals are known to be oxidised via a radical mechanism with formation, depending on the conditions, of peroxides or alkoxides of the corresponding metals. Only preliminary data exist at present concerning the mechanism of the oxidation of organic compounds of transition metals. The oxidation of $(Me_3SiCH_2)_4.Ti(Zr)$ or $(PhCH_2)_4Zr(Hf)$ takes place at a higher rate at −78 °C. For example, the oxidation of $(PhCH_2)_4Hf$ in toluene for 3 min results in the quantitative formation of $(PhCH_2O)_4Hf$. In the presence of an excess of pyridine the initial rate of oxidation of $(PhCH_2)_4Zr(Hf)$ diminishes, one mole of oxygen is then absorbed (at −78 °C), and $(PhCH_2)_2Hf(OCH_2Ph)_2.Py$ is formed[97,98]. The authors suggest that organometallic peroxides are formed in the first stage of the oxidation reaction and either rearrange or react with another molecule of the organometallic compound, giving rise ultimately to alkoxides.

The insertion of elementary sulphur and selenium in the transition metal–carbon σ-bond has been described in only two instances. In contrast to the compounds RMgX, whose interaction with S_8 and Se yields the corresponding mercaptans and selenoalcohols, the compounds Cp_2NbR_2 (R = Me or α-thienyl) give rise to niobium(V) complexes and not insertion products on irradiation with ultraviolet light in benzene in the presence of S_8:[99]

$$Cp_2NbR_2 \xrightarrow[C_6H_6]{S_8,h\nu} Cp_2Nb\begin{matrix}R\\ \diagup\\ \diagdown\\ S\end{matrix}\!\!\begin{matrix}\\ \\ \\ S\end{matrix} .$$

An X-ray diffraction study of the complex $Cp_2Nb(S_2)Me$ showed that S_2 is a bidentate ligand and that the Mb–S distances are 2.515 and 2.432 Å.[100]

Analogously to Grignard reagents, a direct insertion of the Se atom in the M–C σ-bond has been observed for Cp_2MMe_2 (M = Zr or Hf). On refluxing with two equivalents of selenium, the derivatives thus produced give rise to a high yield of $Cp_2M(SeMe)_2$.[101]

2. Reactions with Carbon Monoxide

Numerous studies in this field during recent years established the mechanism of the coordination and subsequent insertion of the CO molecule as a function of the central atom and the character of the σ-substituent. The discovery of these features became possible when the cyclopentadienyl compounds $Cp_2M(R)X$, Cp_2TiR, and Cp_2MR_2 (R = Me, Ph, CH_2Ph, or C_6F_5; M = Ti, Zr, Hf, V, Nb, or Ta; X = Cl or OEt) were used[102–108]. It was established that the first stage involves the coordination of the CO molecule to the central atom. The secondary reactions leading to the final product depend on the nature of the central atom.

We shall consider how this situation arises in the few-reactions of compounds of the type R_nM with CO which have been investigated. The $(PhCH_2)_4Ti$ molecule absorbs only two CO molecules. The highest coordination number of titanium(IV) is six, so that only two ligands can be coordinated to the central atom in $(PhCH_2)_4Ti$ [in the analogous reaction of CO with the complex $(PhCH_2)_4Ti.NH(C_6H_{11})_2$, in which titanium-(IV) has a coordination number of 5, only one mole of CO is absorbed]. The infrared spectrum of the solution shows initially absorption bands at 1952 and 1873 cm^{-1}, which are characteristic of the coordinated CO group: subsequently these bands vanish and new bands due to the carbonyl group $\rangle C{=}O$ appear at 1640 and 1635 cm^{-1}. The acyl derivative $(PhCH_2)_2Ti(COCH_2Ph)_2$ was isolated as a result of the reaction. The process is reversible; when the solution is heated, CO is evolved and the initial compound $(PhCH_2)_4Ti$ reformed[109].

In contrast to $(PhCH_2)_4Ti$, the titanium(II) derivative $(PhCH_2)_2Ti.3Et_2O$ reacts slowly with CO in toluene (p_{CO} = 2 atm) at 20 °C and not more than two moles of CO are absorbed irreversibly. It has been established that 0.5 mole of CO is absorbed after 5 h, 1.0 mole after 10 h, and 2.0 moles after 24 h. The slow insertion is complicated by secondary reactions giving rise to a complex range of products[110].

The compound $(PhCH_2)_4Zr$ reacts with CO in decalin at 22 °C. Analysis of the zirconium-containing products demonstrated the presence of the Zr–CO–CH_2Ph, –Zr–O–C–CH_2Ph, and other fragments[111].

The vanadium(IV) and chromium(IV) compounds $(Me_3Si.CH_2)_4M$ and $(iso\text{-}Pr)_4Cr$ do not react with CO at 20 °C under normal pressure owing to the large bulk of the σ-substituents which obscure the central atom and prevent the coordination of the CO. However, at a CO pressure of 50 atm in THF, all the isopropyl groups are displaced from the $(iso\text{-}Pr)_4Cr$ molecule and $Cr(CO)_6$ is formed[27,112].

When the molybdenum complex $ClMo(CH_2SiMe_3)_3.PMe_3$ is acted upon by CO, two Me_3SiCH_2 groups are substituted by carbonyl groups and some of them migrate to a coordinated CO molecule, giving rise to an η^2-coordinated acyl group. The carbonylation product was identified on the basis of X-ray diffraction data as a dimer with hexacoordinate molybdenum $[ClMo(COCH_2SiMe_3)CO_2(PMe_3)]_2$.[58] The complexes $(C_6F_5)_2Co.2PR_3$ (R = Et, n-Bu, or Ph) combine reversibly with one CO molecule to form the pentacoordinate carbonyl complexes $(C_6F_5)_2Co.2PR_3(CO)$. An excess of CO induces the decomposition of the complexes accompanied by the formation of the dimer $[Co(CO)_3.PR_3]_2$.[113] When the dioxane complex is acted upon by CO, the dioxane is displaced and, in the presence of an excess of CO, cobalt is reduced to cobalt(I):[113]

$$(C_6F_5)_2Co\cdot 2diox \xrightarrow[-78°C]{CO} [(C_6F_5)_2Co(CO)_3] \xrightarrow[20°C]{CO} (C_6F_5)Co(CO)_4 .$$

When a stream of CO is passed through a tetrahydrofuran solution of $(C_6F_5)_2Ni.2diox$ for 8–10 h at 20 °C, the colour of the solution changes and the infrared spectra indicates the presence of a coordinated CO group. However, the attempts to isolate the carbonyl complex led only to the decomposition product $(C_6F_5)_2$ [114] (Table 13).

3. Reactions with Carbon Dioxide

Organolithium and organomagnesium compounds, which behave as sources of carbanions, readily react with various electrophiles, particularly with CO_2. This reaction can be formally represented as the insertion of the carbonyl group in the metal–carbon bond. This results in the formation of lithium or magnesium carboxylates, which give rise to the corresponding carboxylic acids after hydrolysis.

Table 13. Products of the reactions of R_nM with CO_2 and CO (p = 1 atm).

Initial compound	Reagent	Reaction conditions			Reaction products	Yield, %	Refs.
		solvent	t, °C	time, h			
$(PhCH_2)_2Ti\cdot 3Et_2O$	CO_2	THF	20	24	$(PhCH_2CO_2)_2Ti\cdot 3Et_2O$	99	[110]
$(PhCH_2)_4V\cdot 2Et_2O$	CO_2	pentane	0	96	$V(OCOCH_2Ph)_2$	95	[21]
$(PhCH_2)_4V\cdot 2Et_2O$	CO_2	Et_2O	−20	2	$V(OCOCH_2Ph)_3$	99	[21]
$(C_6F_5)_4V\cdot 2Et_2O$	CO_2	THF	20	150	$V(OCOC_6F_5)_3$	95	[21]
$(C_6F_5)_3V.THF$	CO_2	THF	20	150	$V(OCOC_6F_5)_3$	96	[21]
$(Me_2SiCH_2)_3V.THF$	CO_2	THF	−20	3	$V(OCOCH_2SiMe_3)_3$	83	[21]
$Me_2Ni.bipy$	CO_2	benzene	80	15	$Ni(OCOMe)_2\cdot bipy$	90	[117]
$Et_2Ni.bipy$	CO_2	benzene	50	15	$Ni(OCOEt)_2\cdot bipy$	52	[117]
$Et_2Hf[N(SiMe_3)_2]_2$	CO_2	pentane	20	24	$Et_2Hf[OCON(SiMe_3)_2]_2$	90	[78]
$(PhCH_2)_4Ti$	CO	pentane	−50	—[b]	$(PhCH_2)_2Ti(COCH_2Ph)_2$	80	[109]
$(iso\text{-}Pr)_4Cr$	CO	THF	20[a]	—[b]	$Cr(CO)_6$	66	[112]
$ClMo(CH_2SiMe_3)_3\cdot PMe_3$	CO	PE	20	—[b]	$[ClMo(COCH_2SiMe_3)\cdot (CO)_2(PMe_3)]_2$	99	[58]
$(C_6F_5)_2Co\cdot 2diox$	CO	hexane	20	—[b]	$(C_6F_5)Co(CO)_4$	60	[113]

Remarks: [a] p_{CO} = 50 atm; [b] time not indicated.

Systematic studies of the insertion of CO_2 in the transition metal–carbon σ-bond in derivatives of the type R_nM were begun quite recently. It was found that the compound $(PhCH_2)_4M$ (M = Ti or Zr) absorb slowly and irreversibly two moles of CO_2 per gramme-atom of the metal at 20 °C (p_{CO_2} = 13 atm), which is caused, as in the insertion of CO, by the coordinating capacity of Ti(IV) and Zr(IV). The hydrolysis of the reaction products yields in both cases $PhCH_2COOH$ as well as $(PhCH_2)_3COH$ as a result of secondary reactions[5]. The complex $(C_6F_5)_4Ti.2Et_2O$ does not react with CO_2 at 20 °C and p_{CO_2} = 2 atm.[44]

The derivatives R_3Ti (R = CH_2Ph or CH_2SiMe_3) are not carboxylated by gaseous CO_2 in toluene at −70 °C and p_{CO_2} = 1 atm.[21,48] The insertion of CO_2 in the Ti–C_6F_5 bond in $(C_6F_5)_3Ti$ has not been observed either at 20 °C (p_{CO_2} = 2 atm).[48]

It has been observed that, after 24 h at 20 °C (p_{CO_2} = 1 atm), the compound $(PhCH_2)_2Ti.3Et_2O$ absorbs two moles of CO_2 with formation of the complex $(PhCH_2CO_2)_2Ti.3Et_2O$. Analysis of the infrared spectrum showed that the carboxylate group in this complex has the η^1-coordination[110].

Detailed studies have been made of the character of the interaction of CO_2 with a series of vanadium(IV) and vanadium(III) compounds: $(Me_3SiCH_2)_4V$, $R_4V.2THF$ (R = CH_2Ph or C_6F_5), and $R_3V.THF$ (R = CH_2SiMe_3 or C_6F_5).[21] The compounds $(Me_3SiCH_2)_4V$ and $[(Me_3Si)_2CH]_3V$, in which the central atom is shielded, do not absorb CO_2.[21,32] The complexes $(PhCH_2)_4V.2Et_2O$ and $R_3V.THF$ (R = CH_2Ph or CH_2SiMe_3) absorb CO_2 at −20 °C, while $(C_6F_5)_4V.2Et_2O$ and $(C_6F_5)_3V.THF$ react slowly with CO_2 at +20 °C.

Experimental data have shown that at the beginning of the reaction the CO_2 molecule is coordinated to the vanadium atom, which is accompanied by the displacement of the Et_2O or THF ligand species. Subsequently the σ-substituent migrates to the carbon atom with formation of the carboxylate. The multistage insertion of CO_2 in vanadium(IV) and vanadium(III) derivatives as well as the reactions of the carboxylates formed, which behave analogously to the mixed compounds R_nVX_{m-n} examined above, has been investigated[21]. The carboxylation of the test compounds with an excess of gaseous CO_2 leads to the formation of $V(OCOR)_3$. Analysis of the infrared spectra has shown that the carboxylate group in these compounds has the η^2-coordination (Table 13). The reactivity with respect to CO_2 of the remaining σ-derivatives described above in Section II has not been investigated. There are in the literature isolated examples of the insertion of CO_2 in the M–C σ-bonds in metal complexes (M = Mn, Fe, or Ni). For example, after reaction with CO_2 (20 °C, 2 h), $[R_3Mn]^-Li^+$ and $R_3MnMgCl$ give rise to RCO_2H (R = Ph or Mes) in quantitative yields after hydrolysis[115]. The complex $(Me_3P)(H)Fe(CH_2PMe_2)$ reacts with CO_2 in THF at 20 °C and yields an unusual product of insertion in the Fe–C bond[116]. The nickel derivatives $R_2Ni.bipy$ (R = Me or Et) readily absorb two moles of CO_2 with formation of the carboxylates $(RCO_2)_2Ni.bipy$.[117]

Thus the results obtained hitherto demonstrate that the general character of the reactions with CO_2 is the same for the organic compounds R_nM of lithium, magnesium, and transition metals. It is noteworthy that the reactivity of the transition metal–carbon σ-bond depends on the nature and valence of the metal and also on the character of the σ-substituent.

It has been shown in relation to $Et_2Hf[N(SiMe_3)_2]_2$ that, when M–C and M–N bonds are present in the molecule, CO_2 is inserted in the M–N bond with formation of $Et_2Hf[OCON.(SiMe_3)_2]_2$.[78,118]

4. Reactions with Aldehydes and Ketones

The addition of organolithium and organomagnesium compounds to the carbonyl group in aldehydes and ketones is one of the most important reactions in organic synthesis. The study of such reactions involving transition metal complexes is only just beginning.

It has been observed that $(PhCH_2)_4Ti$ readily interacts with one or two equivalents of ketones (acetone, benzophenone), yielding after hydrolysis the corresponding tertiary alcohols; the excess ketones do not react[119]. The reaction of $(PhCH_2)_2.Ti.3Et_2O$ with the above ketones results in the formation of the alkoxides $Ti[OCR_2(CH_2Ph)]_2$ (R = Me or Ph), which do not contain coordinated ether[110].

The reactivity of compounds of the type $R_nTi(OR')_{4-n}$ with respect to carbonyl compounds is lower than that of R_nTi. For example, $(PhCH_2)_2Ti(OME)_2$ does not react with acetone; one refluxing in Et_2O for 7 h, $PhTi(OPr\text{-}iso)_3$ reacts with PhCO to yield 19% of Ph_3COH after hydrolysis. At 20 °C the compound $PhTi(OPr\text{-}iso)_3$ reacts only with aldehydes[66,120,121]. Investigations have shown that the compounds $RTi(OPr\text{-}iso)_3$ (R = Bu or Ph) are more selective in relation to carbonyl compounds than the corresponding organolithium compounds [120–122]. In contrast to $PhTi(OPr\text{-}iso)_3$, $MeTi(OR')_3$ reacts with different ketones[120,123].

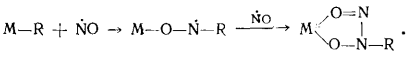
Like $(PhCH_2)_4Ti$, the compound $(PhCH_2)_4V$ reacts only with two moles of acetone, forming $(PhCH_2)_2V[OC(Me)_2CH_2Ph]_2$. It is known that $R_2V(OBu\text{-}t)_2$ derivatives do not react with acetone even on heating[21].

The data obtained for the titanium and vanadium compounds make it possible to put forward a general reaction mechanism. Analogously to organolithium and organomagnesium compounds, in the first stage oxygen is coordinated to the metal.

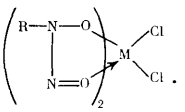
The alkoxy-groups formed are very bulky and tend to associate. These findings indicate the shielding of the central atom, so that coordination to the latter of other ketone molecules becomes virtually impossible. Steric effects are also responsible for the inertness of the compounds $R_2M(OR')_2$ (M = Ti or V) and $PhTi(OPr\text{-}iso)_3$ in relation to ketones. Bulky alkoxy-groups displace the coordinated Et_2O molecules from $(PhCH_2)_2Ti.3Et_2O$ in the alkoxide formation stage.

5. Reactions with Nitric Oxide

The mode of reaction with NO is determined by the nature of NO itself, which is a radical. Reactions with diamagnetic complexes lead to the formation of *N*-alkyl-*N*-nitrosohydroxylaminate derivatives[124]:

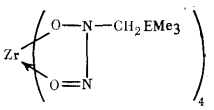


The compounds R_2MCl_2 (R = CH_2CMe_3 or CH_2SiMe_3; M = Ti or Zr) absorb four moles of NO in petroleum ether at 0 °C and give rise to octahedral complexes:



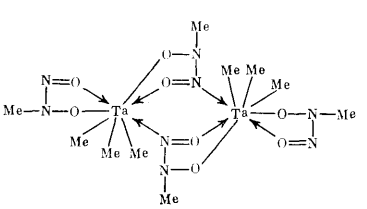
Analysis of the infrared spectra of these complexes indicates the *cis*-disposition of the Cl atoms relative to the metal atom and also the η^2-coordination of the two ON(R)NO groups. The compound $(Me_3CCH_2)_3TiCl$ absorbs six moles of NO, while $(Me_3SiCH_2)_4Ti$ absorbs eight moles of NO. Since titanium forms only hexacoordinate complexes, the ON(R)NO groups in the complexes are probably not equivalent; for example, $Ti[ON(CH_2SiMe_3)NO]_4$ has two chelate and two monodentate groups.

The reaction of $(Me_3ECH_2)_4Zr$ (E = C or Si) with NO results in the formation of monomeric octacoordinate complexes which are stable in air:



The observed difference between the structures of the products obtained from titanium and zirconium compounds is due to the different coordinating capacities of the above metal atoms.

Octacoordinate complexes are formed as a result of the reaction of Me_5Nb or Me_5Ta with NO. However, the nature of the central atom permits the existence of different structures of these metal complexes. It has been found that Me_5Nb gives rise to the monomeric complex $Me_2Nb[ON(Me)NO]_3$ with equivalent chelate ligands. A dimeric complex is formed from Me_5Ta and the following structure has been attributed to it on the basis of infrared and NMR spectra:



The paramagnetic complexes of transition metals with an unpaired electron at the metal atom react with NO to produce oxo-derivatives of the metals and azomethane[124]. The hypothesis that the initial stage in the reactions of paramagnetic complexes with NO involves the coordination of the NO molecule to the transition metal atom has been confirmed by the isolation of the complex $[(Me_3Si)_2CH]_3CrNO$, in which bulky ligands prevent further reactions[32].

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It follows from the results of the analysis of the investigations carried out that considerable progress has now been achieved in the chemistry of the thermally stable σ-derivatives of transition metals. Extensive studies of the properties of the compounds R_nM and R_nMX_{m-n} have made a definite contribution to the development of theoretical organoelemental chemistry. The research prosecuted vigorously on these lines gives rise to good prospects for the practical utilisation of the σ-derivatives in metal complex catalysis, in the formation of biologically active preparations, and in the development of new methods for the preparation of protective coatings by the decomposition of organometallic compounds.

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Platinum Metal Fluorides

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The properties of the simple fluorides, oxide fluorides, and dioxygenyl compounds of the platinum metals have been reviewed. The most important fields of application and directions of study in the field of platinum metal fluorides have been outlined. The bibliography contains 185 references.

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I. INTRODUCTION

The platinum metals are now widely used in chemical technology, chiefly as catalysts in petroleum reforming, and also in electrical technology, jewellery, and laboratory practice. The use of platinum metals as alloy components makes it possible to improve considerably the mechanical properties and increase the corrosion resistance of alloys, compared with the pure metals.

The fields of application of the platinum metal fluorides are determined directly by their physicochemical properties. The development of fluoride metallurgy is extending the possible applications of the volatile platinum metal fluorides in one of the most promising fields—the preparation of coatings, powders, alloys, or articles by reducing the volatile fluorides with hydrogen. For example, the preparation of iridium coatings by reducing IrF_6 with hydrogen has been described[1,2]. The simultaneous reduction of fluorides can be used to prepare alloys of platinum metals with refractory metals. The use of platinum metal fluorides to regenerate spent catalysts in the petrochemical industry appears promising[3].

Increasing quantities of platinum metals are accumulating in spent nuclear fuel, which can possibly be processed by subliming the fluorides. It has been estimated[4] that for 3% burnout, one ton of nuclear fuel gives 500 g of Rh and 1500 g of Pd. By the year 2000, the quantity of palladium produced in the reactors of atomic power stations will be about 250 tons, close to the required quantity of this metal. The quantities of rhodium and ruthenium obtained by nuclear fission will exceed the expected demand. Here it is necessary to solve the problem of removing the radioactive isotope ^{103}Ru,[5] and then the problem of isolating the other platinum metals.

The electronic configuration of the atoms Ru ($4d^75s^1$), Rh ($4d^85s^1$), Pd ($4d^{10}$), Os ($5d^66s^2$), Ir ($5d^76s^2$), and Pt ($5d^96s^1$) makes possible a variety of fluoride compounds, in which the oxidation state of the metal varies from +2 to +8. Simple platinum metal fluorides have coordination numbers from 2 to 7.

Thus platinum metal fluorides are already of considerable interest in both technology and chemistry.

Published reviews of the properties of platinum metal fluorides[6,7] are based on 15–20-year-old publications, and require to be bought up to date. A number of recent books and reviews have dealt with platinum metal fluorides among other fluorides[8–12], but they deal mainly with the properties of the fluorides of individual platinum metals, for example ruthenium,[9,12] iridium,[10] and osmium.[11] Data on the properties of fluorides are given in a number of reference books[13–16], but even the most complete of these[16] includes original publications only up to 1973.

The aim of the present review was to systematise the methods of synthesis, review published data on the physicochemical properties of the platinum metal fluorides, and define the most important directions of studies in this field.

II. SIMPLE FLUORIDES

1. Higher Fluorides

Among the platinum metals, a heptafluoride is known only for osmium. The higher fluoride OsF_7 was obtained by treating osmium powder with fluorine at 573–683 K and a pressure of 350–400 atm in a nickel bomb[17]. Osmium heptafluoride is obtained as a pale-yellow extremely hygroscopic powder, which partly loses fluorine at temperatures above 173 K, and on prolonged standing at room temperature decomposes quantitatively to OsF_6 and fluorine. Osmium heptafluoride has been characterised by mass spectrometry, magnetic susceptibility, and EPR and infrared spectroscopy at 93 K. The wavenumbers of vibrational bands in the infrared spectrum of OsF_7 are 715, 550, 483, 366, 336, and 282 cm^{-1}. Analysis of the infrared spectrum indicates that the OsF_7 molecule has D_{5h} symmetry[17]. A comparison of the enthalpies of formation of the fluorides of the elements from Hf to Re has been used to estimate the enthalpies of formation of gaseous OsF_7 and the hypothetical OsF_8: −1140 kJ $mole^{-1}$ and −980 kJ $mole^{-1}$ respectively[18].

The reported formation of RuF_8 [19] by the fluorination of ruthenium and its dioxide has not been confirmed. A study of the hydrolysis of ruthenium fluorides and the fluorination of ruthenium hydroxides revealed the formation of a volatile substance[20], whose infrared spectrum showed bands at 389 cm^{-1} and 1030 cm^{-1}, previously assumed erroneously[19] to be ruthenium octafluoride. This substance is the adduct $RuO_4(HF)_{10}$, which volatilises at temperatures above 273 K and an HF pressure above 150 mmHg.[20]

The most fully characterised platinum metal fluorides are the hexafluorides, of which only palladium hexafluoride was isolated only recently[21] and has been little studied. A general method for obtained the hexafluorides of ruthenium[22], rhodium[23], osmium[24], and iridium[25] involves the action of fluorine, diluted with nitrogen, on the metal powders, heated to 550–700 K, with subsequent rapid cooling of the reaction products. Platinum hexafluoride is obtained similarly, but under more severe conditions, by heating platinum wire electrically in a stream of fluorine to 1150–1300 K.[26,27] The synthesis of PtF_6 by the action of fluorine on spongy platinum at a pressure of 15 atm and a temperature of 470 K and a molar

ratio Pt : F_2 = 1 : 15, which gives a yield of 75%, has also been proposed[28].

A method for obtaining platinum metal hexafluorides in solution in KrF_2, anhydrous HF, or BrF_5 has been successfully developed and applied[29]. The solution of the metals, oxides, or lower fluorides in KrF_2 gives complexes $KrF_2.MF_5$ (M = Pt, Ru, Rh) and $KrF_2.2MF_5$ (M = Pt, Ru), which when heated slightly decompose vigorously with the quantitative formation of the corresponding metal hexafluorides, Krypton difluoride has a high fluorinating power, and acts as a fluoride ion donor, stabilising the higher oxidation states of the elements.

An effective method for the synthesis of thermally unstable platinum metal hexafluorides involves the use of atomic fluorine[30], which takes part in chemical reactions with an activation energy close to zero. The reaction of atomic fluorine with palladium powder at room temperature was in fact used to prepare PdF_6.[21] The fluorination of the platinum metals by atomic fluorine at low temperatures (below 370 K) is rapid. The yield of hexafluorides decreases in accordance with their thermal stability in the order OsF_6 > IrF_6 > PtF_6 > RuF_6 > RhF_6, and also depends on the composition of the starting material. The limiting stage of the fluorination of the platinum metals by atomic fluorine is the conversion of the pentafluorides to the hexafluorides. The fluorination of osmium and iridium oxides by atomic fluorine also gives the hexafluorides of these metals.

Table 1. Physical properties of platinum metal hexafluorides.

Property	RuF_6 [22, 34]	PhF_6 [23, 34]	OsF_6 [18, 24, 34, 35]	IrF_6 [25, 34, 35]	PtF_6 [27]
Colour*	dark brown	black	yellow	pale yellow	dark red
M.p., K	327	343	305.2 306.55	317.25	334.45
B.p., K	—	346.65	320.65	326.75	342
$T_{p.t.}$, K	275.65	250.2	272.75	271.95 273.55	276.45
ΔH^0 of formation in the gaseous state at 298.15 K, kJ mole^{-1}	—	—	−1080 ** [18]	−850 ** [37]	−600 *** [36]
ΔH^0_{fusion}, kJ mole^{-1}	—	—	7.4 ****	5.0	4.5
$\Delta H^0_{volatilisation}$, kJ mole^{-1}	—	—	28.1	30.9	29.5
$\Delta H^0_{phase\ transformation}$, kJ mole^{-1}	—	—	8.2	7.1	9.0
$\Delta H^0_{sublimation}$, kJ mole^{-1}: above the phase transformation	38.5	41.0	35.5	35.9	38.9
below the phase transformation	—	—	43.7	43.0	47.9
ΔS^0_{fusion}, J mole^{-1}K^{-1}	—		23.9 ****	15.6	13.4
$\Delta S^0_{volatilisation}$, J mole^{-1}K^{-1}	—	121	87.9	94.6	86.2
$\Delta S^0_{phase\ transformation}$, J mole^{-1}K^{-1}	—	—	30.1	26.0	32.6

*PdF_6 is dark red[21]. **Estimated data. ***At 915 K, ****These data are probably too high.

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

A study of the kinetics of the reaction of compact Ir and Pt with atomic fluorine in the range 1000–1450 K for iridium and 600–1430 K for platinum at a partial pressure of atomic fluorine of 0.005–0.06 mmHg [31] showed that the condensed films of lower fluorides of iridium and platinum formed on the metal surfaces do not decrease the rate of fluorination. The fluorination of osmium powder by molecular fluorine[32] takes place in two stages, and is described satisfactorily by the equation for a contracting sphere. The activation energy is 55.5 ± 2.1 kJ mole^{-1} for the first stage, and 17.4 ± 5.4 kJ mole^{-1} for the second. The order of the reaction is 0.5, so that it is assumed that the limiting stage of the fluorination of osmium is the dissociative adsorption of fluorine on the metal surface. The kinetics of the fluorination of ruthenium powder by molecular fluorine[33] in the temperature range 543 to 583 K at a fluorine partial pressure of 22.5–60 mmHg differs from that of the fluorination of osmium. This process is a single-stage process, the activation energy is 79.5 ± 7.1 kJ mole^{-1}, and the order of the reaction with respect to fluorine is 1. The rate of fluorination of ruthenium increases if the metal powder is heated beforehand in hydrogen.

The principal physical properties of the platinum metal hexafluorides are given in Table 1. The boiling points (T) and the enthalpies (ΔH^0) and entropies (ΔS^0) of fusion, volatilisation, phase transformation, and sublimation of the hexafluorides were obtained from the temperature dependence of the vapour pressure.

Linear correlations have been established between the enthalpies of fusion and volatilisation of the hexafluorides of W, Re, Os, Ir, and Pt and their melting and boiling points respectively[37,38]. The correlation of the enthalpy of fusion with the melting point indicates that the value of the enthalpy of fusion of OsF_6 given in Table 1 (7.5 kJ mole^{-1}) is about 2.7 kJ mole^{-1} too high. The value of the entropy of fusion of OsF_6 is also apparently too high. The correlation of the logarithms of the absolute values of the enthalpies of formation of the gaseous hexafluorides of W, Re, Os, and Pt with the stretching vibration frequency ν_1 was used[37] to estimate the enthalpy of formation of gaseous IrF_6 at 298.15 K—approximately −850 kJ mole^{-1}.

The hexafluorides crystallise in a body-centred cubic lattice at room temperature, and in an orthorhombic lattice at low temperatures[34]. The low-temperature form has the YF_3 structure, space group *Pnma*, and the number of formula units Z in the unit cell is 4. The high-temperature form (298 K) is isostructural with the cubic MoF_6 phase, Z = 2. The lattice parameters and densities for both phases of each hexafluoride are given in Table 2.

Table 2. Structural characteristics and densities of the crystals of the platinum metal hexafluorides[34].

Substance	Calculated density of the crystal, kg m^{-3}		Lattice parameters, A	
	cubic phase	orthorhombic phase	cubic phase	orthorhombic phase
RuF_6	3130	3500	6.11±0.01	*a* 9.44 *b* 8.59 *c* 4.98
RhF_6	3130	3620	6.13±0.02	*a* 9.40 *b* 8.54 *c* 4.96
OsF_6	4130	4770	6.25±0.02	*a* 9.59 *b* 8.75 *c* 5.04
IrF_6	4200	4820	6.23±0.02	*a* 9.58 *b* 8.73 *c* 5.04
PtF_6	4280	4900	6.21±0.02	*a* 9.55 *b* 8.71 *c* 5.03

The saturated vapour pressure over RuF_6 at 273.2, 277.8, 281.8, 284.2, 287.6, and 290.8 K has the values 23, 32, 40, 46, 56, and 67 mmHg,[22] and that over RhF_6 at 273, 278, 284, 289, and 293 K has the values 15, 19, 29, 40, and 49.5 mmHg respectively[23]. The vapour pressure (p, mmHg) is described

by the equations

for OsF_6 [35] $\lg p = 10.290 - 2284/T$ ($233.15 \leqslant T \leqslant 272.75$ K)
$\lg p = 8.726 - 1857.7/T$ ($272.75 \leqslant T \leqslant 307.15$ K)
$\lg p = 7.470 - 1472.8/T$ ($307.15 \leqslant T \leqslant 320.65$ K)

for IrF_6 [35] $\lg p = 10{,}000 - 2245.7/T$ ($223.15 \leqslant T \leqslant 273.55$ K)
$\lg p = 8.618 - 1867.5/T$ ($273.55 \leqslant T \leqslant 317.15$ K)
$\lg p = 7.952 - 1656.5/T$ ($317.15 \leqslant T \leqslant 327.15$ K)
for PtF_6 [27] $\lg p = 27.7758 - 3147.6/T - 6.09 \lg T$
($250.2 \leqslant T \leqslant 276.15$ K)
$\lg p = 20.6280 - 2528.7/T - 4.080 \lg T$
($276.15 \leqslant T \leqslant 334.45$ K)
$\lg p = 89.1496 - 5685.8/T - 27.485 \lg T$
($334.45 \leqslant T \leqslant 354.9$ K).

The vibrational spectra of the platinum metal hexafluorides have been the subject of a large number of experimental studies[23,39-42]. All the platinum metal hexafluorides have a regular octahedral configuration (O_h symmetry). For RuF_6 and OsF_6 the ν_2 and ν_5 frequencies are anomalously low, because of the dynamic Jahn–Teller effect[39-41]. The non-perturbed values of these frequencies were calculated for the first time[43] by interpolation from the dependence of the vibrational frequencies on the number of non-bonded electrons in the hexafluorides.

In this and later papers[44-47], the infrared and Raman spectroscopic data for the platinum metal hexafluorides were analysed and systematised.

The calculated vibrational frequencies in the infrared and Raman spectra of the platinum metal hexafluorides[43] and the interatomic distances (r_{M-F}), determined using Badger's rule[48,54], are given to Table 3. The force constants and mean-square amplitudes of the vibrations of the M–F bonds have been calculated[48,50-55].

Table 3. Calculated molecular constants of platinum metal hexafluorides[43].

Substance	Vibrational wavenumbers in the spectra of MF_6, cm^{-1}						r_{M-F}, Å
	ν_1 (a_{1g})	ν_2 (e_g)	ν_3 (f_{1u})	ν_4 (f_{1u})	ν_5 (f_{2g})	ν_6 (f_{2u})	
RuF_6	675	624	735	275	283	186	1.8775
RhF_6	634	595	724	283	269	192	1.8738
PdF_6	590	525	711*	280	258	191	1.87
OsF_6	730.7	668	720	268	276	205	1.831 (1.831±0.008 **)
IrF_6	701.7	645	719	276	267	206	1.833 (1.830±0.008 **)
PtF_6	656.4	601	705	273	242	211	1.829

*This band has been detected in the infrared spectrum of PdF_6.[21]
**Determined by electron diffraction in the gaseous state[49].

The ^{19}F NMR spectra of the hexafluorides of osmium, iridium, and platinum[56,57] show that in the low-temperature orthorhombic phase there is tetragonal distortion of the octahedra of the hexafluorides, and the chemical shifts of the axial and equatorial F atoms in PtF_6 are apparently the highest for all known fluoride compounds.

Thermochemical data[58,59] indicate that the electron affinity increases in the order $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$, and for PtF_6 it is greater than 653 kJ $mole^{-1}$ (6.8 eV); the difference between two neighbouring terms is approximately constant, 84 kJ $mole^{-1}$ (0.9 eV). The spectra of the charge-transfer complexes between IrF_6 and liquid xenon in the near infrared range[60] have been used to estimate the electron affinity of IrF_6, 548.1 kJ $mole^{-1}$ (5.7 eV), which is close to the value obtained by other workers[58,59]. The electron affinity of PtF_6 at 0 K, calculated from effusion measurements, lies between 5.14 eV and 7.9 eV.[36] The physical properties and bonds in the molecules of the hexafluorides of osmium, iridium, and platinum have been studied theoretically[61-63]; earlier measurements of the electron affinity were examined critically, and new measurements of this quantity carried out[63]. The calculated values of the electron affinity and ionisation potentials of OsF_6, IrF_6, and PtF_6 are given in Tables 4 and 5. The values of the ionisation potentials of OsF_6 [62] are close to the data previously obtained from the photoelectron spectra[64].

Table 4. Electron affinity of MF_6, eV.

M	Model I (Ref.62)	Model II (Ref.62)	Published data (Ref.63)
Os	6.17	5.97	7.19 *
Ir	6.96	6.86	8.24 *
Pt	7.59	8.55	9.3

*Values calculated assuming a constant increment per unit increase in the atomic number[65].

Table 5. Ionisation potentials of MF_6, eV.

Configuration	OsF_6		IrF_6 [62]	PtF_6 [62]
	[62]	[64]		
$2t_{2g}$	12.93	14.1	13.72	15.28
$1t_{1g}$	15.48	14.8	15.40	16.18
$3t_{1u}$	15.80	15.5	15.75	16.45
$1t_{2u}$	15.99		15.88	16.65
$2t_{1u}$	16.39	16.5	16.40	17.09
$2a_{1g}$	17.16	16.9	17.21	17.68
$1t_{2g}$	18.55	18.7	18.85	20.16
$2e_g$	20.17	19.6	20.40	21.53

In spite of the fact that the hexafluorides of the platinum metals are often considered as a whole, their chemical properties show significant differences[66]. The hexafluorides of all the platinum metals except Os and Ir are thermally unstable and begin to decompose even at room temperature with the liberation of fluorine[22,23,67,68]; the rate of decomposition of PdF_6 under these conditions is much greater than that of the other hexafluorides, and amounts to 30% h^{-1}.[21] The tendency for the hexafluorides to decompose increases with increase in atomic number in each series, and the stability decreases more rapidly in the second than in the third series[6,69].

RuF_6 and RhF_6 react with Pyrex even at room temperature; the reaction with quartz is slower[22,23]; when heated with Pyrex, OsF_6 apparently forms OsO_3F and OsO_2F_2;[70] IrF_6 does not react with Pyrex up to 420 K,[25] but at 620 K it is reduced quantitatively by finely divided glass to iridium pentafluoride[68]; PtF_6 also decomposes slowly in contact with Pyrex or quartz[26].

The platinum metal hexafluorides are readily hydrolysed by even traces of moisture, undergoing disproportionation or reduction to give various products. For RuF_6 the chief product is $RuO_2.nH_2O$;[22] the hydrolysis of PdF_6 also gives the hydrated dioxide $PdO_2.nH_2O$, with the liberation of oxygen and ozone[21]. OsF_6 is hydrolysed according to equations[24]:

$$2OsF_6 \rightarrow OsF_6^{2-} + Os^{8+} + 6F^-,$$
$$OsF_6 + H_2O \rightarrow OsF_6^{2-} + 0.5O_2 + 2H^+.$$

The hydrolysis of IrF_6 gives $IrO_2.nH_2O$, with the liberation of ozone[25]; a PtF_6 specimen weighing less than 200 mg gives a yellow solution of H_2PtF_6 ($PtF_6 + H_2O \rightarrow H_2PtF_6 + 0.5O_2$), and quantities of more than 1 g give a black precipitate[27].

A study of the hydrolysis of solutions of platinum metal hexafluorides in hydrogen fluoride by accurately measured quantities of H_2O [71] showed that the products are the oxide tetrafluoride $OsOF_4$ for OsF_6, and for RuF_6, IrF_6, and PtF_6 the hydroxonium salts $H_3O^+MF_6^-$, or $(H_3O^+)_2PtF_6^{2-}$ for PtF_6 in an excess of H_2O. The hydrolysis of RhF_6 gives an unstable product, which could not be characterised. The difference between the results of the hydrolysis of OsF_6 and the hexafluorides of ruthenium, iridium, or platinum can be attributed to the greater electron affinity of the latter[71].

The reaction of the platinum metal hexafluorides with NO and NOF in most cases gives the ionic compounds $NO^+MF_6^-$.[58,72] In an excess of NOF, RhF_6 and PtF_6 give the salts $(NO)_2RhF_6$ and $(NO)_2PtF_6$.[72] With NO_2F and N_2O_4 with slow heating from 77 K to 298 K, platinum hexafluoride gives NO_2PtF_6 and $N_2O_3PtF_6$ respectively[73].

A study of the behaviour of the hexafluorides of osmium, iridium, ruthenium, and rhodium in redox reactions showed that OsF_6 and IrF_6 react vigorously with PF_3 with considerable liberation of heat to give mixtures of the metals, lower fluorides, and volatile PF_5.[74,75] In anhydrous HF at low temperatures, $Os(PF_3)_2F_4$ and IrF_4 were obtained, and for ruthenium the polymeric compound $[Ru(PF_3)_4]_n$ The hexafluorides OsF_6, IrF_6, and RuF_6 in anhydrous HF oxidise AsF_3 to AsF_5, forming adducts; Os is reduced to Os^V, and Ir and Ru to Ir^{IV} and Ru^{IV}. Unlike OsF_6, which does not react with SbF_3, iridium and ruthenium hexafluorides oxidise it at room temperature to SbF_5, and are converted mainly to the corresponding pentafluorides. Ruthenium hexafluoride oxidises BiF_3 to BiF_5 (this does not take place with OsF_6 and IrF_6) and oxidises ClF_3 to ClF_5, giving a mixture of $ClF_3.RuF_5$ and $ClF_5.RuF_5$.[75] The hexafluorides of osmium, iridium, and ruthenium react with CS_2 to give CF_4 and SF_4; and with hydrogen or the corresponding metal in anhydrous HF to give the pentafluorides; when heated to 370 K they are reduced by hydrogen in the presence of anhydrous HF to the metals[75]. RuF_6 also reacts with xenon[76]; with B_2O_3, ruthenium and iridium hexafluorides give the corresponding pentafluorides, and OsF_6 gives the oxide tetrafluoride $OsOF_4$.[77]

The few chemical reactions reported for RhF_6 do not make it possible to distinguish its oxidising power from that of RuF_6; however, since rhodium hexafluoride is thermally less stable than RuF_6,[6] it may be expected that it will be a stronger oxidising agent. Summarising all the above reactions, Burns and O'Donnell[75] arranged the hexafluorides in order of decreasing oxidising power: $RhF_6 > RuF_6 > IrF_6 > OsF_6$. This trend, which can be explained from thermodynamic data and an examination of the physical properties[6, 65,69,78,79], is confirmed by the data of other workers[74–77]. The oxidising power also increases in the transition metal sub-groups: $RuF_6 > OsF_6$; $RhF_6 > IrF_6$ (RhF_6 oxidises Xe,[76] but IrF_6 does not). PdF_6, prepared only recently, is also a very strong oxidising agent, apparently stronger than PtF_6 and RhF_6. Palladium hexafluoride is rapidly reduced on metal surfaces, and oxidises oxygen and xenon[21].

Platinum hexafluoride occupies a unique position, since it was used to synthesise the ionic compound $O_2^+PtF_6^-$ for the first time[80,81]. Bartlett, drawing attention to the similarity in the ionisation and potentials of xenon and oxygen, carried out the reaction of PtF_6 with Xe and obtained the yellow ionic solid $Xe^+PtF_6^-$, and discovered the chemistry of the noble gases[82]. Platinum hexafluoride reacts with KrF_2 at 273 K to give $KrF^+PtF_6^-$, whose Raman spectrum confirms its ionic structure[83]. The plutonium fluorides PuF_3 and PuF_4, when treated with PtF_6 below room temperature, are converted into PuF_6,[84] ClF_3 into ClF_5,[85] BrF_3 into BrF_5, and Np into NpF_6.[27] An infrared and NMR spectroscopic study of the solid product of the reaction of PtF_6 with $XeOF_4$ [86] showed that this reaction is accompanied by the formation of XeF_5^+, and the oxygen displaced from $XeOF_4$ is converted into O_2^+.

$OsCl_5$ was obtained for the first time by the reaction of OsF_6 with an excess of BCl_3 below room temperature[87]. The reaction of OsF_6 with liquid Br_2 gives solid $Br_2^+OsF_6^-$, and the dissolution of OsF_6 in liquid Cl_2 at 195 K gives a blue solution, from which a green solid of unknown composition separates on cooling[88].

The platinum metal hexafluorides are soluble in anhydrous HF; at 298 K the solubility of OsF_6 in hydrogen fluoride is 0.97 mole in 1000 g.[89]

An EPR study of the homogeneous recombination of fluorine atoms in OsF_6 and IrF_6 molecules at 293 K showed that the rate of recombination in these hexafluorides is the same as that of fluorine atoms in the MF_6 molecules for M = Os, Ir, and W.[90]

The reaction of volatile fluorides with graphite is now attracting considerable interest. Thus treatment of pyrolytic graphite with osmium and iridium hexafluorides gives the compounds $C_8^+OsF_6^-$ and $C_8^+IrF_6^-$, and the insertion of PtF_6 into graphite gives $C_{12}^{2+}PtF_6^{2-}$.[91] The electrical conductivity of the products of the insertion of OsF_6 and IrF_6 along the basal plane of graphite is a maximum for a composition of approximately $C_{24}MF_6$, for which it is 10 times that for the starting material; further insertion leads to a marked decrease in the electrical conductivity (the electrical conductivity of C_8MF_6 is comparable with that of the original graphite). This behaviour differs from that of graphite—AsF_5 systems, in which there is a steady increase in conductivity along the basal plane of graphite with increase in the AsF_5 concentration. The products of the insertion of PtF_6 into graphite are weakly conducting[91]. Examination of structural data and the physicochemical properties of platinum metal hexafluorides shows that they resemble to a considerable extent the hexafluorides of such metals as molybdenum, technetium, tungsten, and rhenium, they all form cubic crystals at room temperature, and orthorhombic crystals on cooling, with similar lattice parameters. The enthalpies of fusion and volatilisation have similar values (kJ $mole^{-1}$): 4.3 and 28.0 respectively for MoF_6; 4.5 and 30 for TcF_6; 4.1 and 25.9 for WF_6; and 4.5 and 28.3 for ReF_6.[16] All these hexafluorides have a regular octahedral configuration and approximately the same interatomic distances (from 1.82 Å in MoF_6 to 1.877 Å in RuF_6).

The main difference between the platinum metal hexafluorides and the corresponding compounds of molybdenum, technetium, tungsten, and rhenium is the higher reactivity of the former. This is revealed in the thermal instability of the platinum metal hexafluorides and in their more extensive hydrolysis (the platinum metal hexafluorides react with water to form the M^{IV} oxides, and MoF_6 and WF_6 give MoO_3 and WO_3 respectively). The platinum metal hexafluorides are also stronger oxidising agents than MoF_6, TcF_6, WF_6, and ReF_6; thus RuF_6, RhF_6, PtF_6, and PdF_6 oxidise even Xe, and platinum and palladium hexafluorides also oxidise oxygen.

2. Pentafluorides

The methods used to prepare the pentafluorides to a large extent are specific for each platinum metal. Pure ruthenium pentafluoride was first obtained by decomposing in a vacuum at 390 K the compound $RuBrF_8$, formed by the reaction of metallic ruthenium with BrF_3 at room temperature[92]. Ruthenium pentafluoride has also been synthesised by the direct fluorination of ruthenium powder with a mixture of F_2 and N_2 at 550–570 K,[93] by a mixture of HF and F_2 diluted with N_2,[94] and by fluorine at 470 K and a pressure of 4–5 atm in a nickel bomb[95].

The pentafluorides of ruthenium, osmium, and iridium have been obtained by the reaction of a solution of XeF_2 in anhydrous HF with $RuCl_3$ or RuO_2, or metallic Os or Ir.[96]

Rhodium pentafluoride is formed, together with RhF_6 and RhF_3, when rhodium wire burns in fluorine, and pure RhF_5 is obtained at a fluorine pressure of 6 atm and a temperature of 670 K.[97]

The reaction of $W(CO)_6$ with an excess of OsF_6 at 273 K gives a mixture of OsF_5, OsF_4, and Os, which can be separated by vacuum distillation (OsF_5 distils at 390 K).[67] Osmium pentafluoride is obtained by reducing OsF_6 with a solution of iodine in IF_5 [67,98] or by tungsten heated to a dull red heat[99].

IrF_5 and OsF_5 have been obtained in 100% yield by reducing IrF_6 and OsF_6 by hydrogen or Si powder in anhydrous HF at 298 K.[100–102] The rate of the process is increased when Pt gauze and ultraviolet irradiation are used. Iridium pentafluoride has been obtained[68] by heating a stoichiometric mixture of the elements in a Monel bomb; the bottom of the bomb was heated to 620–650 K, and yellow crystals of IrF_5 condensed on the lid of the reaction vessel.

Table 6. Physical properties of platinum metal pentafluorides.

Substance	RuF_5 [91, 105]	RhF_5 [97]	OsF_5 [67, 106]	IrF_5 [68]	PtF_5 [103, 107–109]
Colour	emerald-green	dark red	greenish-blue	yellow	dark red
M.p., K	358	368,65	343	378	353
B.p., K	500 *, 503	—	499 *, 506	—	573–578
$\Delta H^\circ_{formation}$, kJ mole^{-1}	−892.9±1.5**	—	—	—	−545 ***
$\Delta H^\circ_{volatilisation}$, kJ mole^{-1}	56.5	—	59.4	—	—
$\Delta S^\circ_{volatilisation}$, kJ mole^{-1}	113.0	—	119.1	—	—
Magnetic moment at room temperature μ, B.M.	3.6	2.93	2.06	1.3	2.05

*Determined by extrapolation from the temperature dependence of the vapour pressure.

**For crystalline RuF_4 at 298.15 K.

***At 915 K.[36]

The fluorination of spongy platinum or $PtCl_2$ by fluorine at 620 K gives PtF_5, which is readily separated from the more volatile O_2PtF_6 by vacuum distillation at 370 K.[80,103] The fluorination can be carried out under pressure[104].

The principal physical properties of the platinum metal pentafluorides are given in Table 6.

All the platinum metal pentafluorides form monoclinic crystals with the RuF_5 structure, space group $P2_1/c$, $Z = 8$. The unit cell parameters and densities of the crystalline platinum metal pentafluorides are given in Table 7.

X-Ray diffraction has shown that the structural unit of the platinum metal pentafluorides is an $(MF_5)_4$ tetramer with bridging F atoms in the *cis*-position. The metal has distorted octahedral coordination; each M atom is surrounded by six F atoms, but two *cis*-F atoms in the MF_6 group are joined to other M atoms. The average M–F distances for the terminal and bridging fluorine atoms are 1.81 Å and 2.01 Å respectively, and the MFM angle is 135°.[95,97,98,110,111] An analysis of the ^{19}F NMR spectra of the platinum metal pentafluorides in the temperature range 77–296 K confirmed that these compounds are polymeric[112].

Table 7. Structural characteristics and densities of the crystals of the platinum metal pentafluorides.

Substance	RuF_5 [98]	RhF_5 [97]	OsF_5 [98]	IrF_5 [98]
Lattice parameters, A angle F–M–F, °	*a* 5.42 * *b* 10.01, *s* 12.47 β 99.82	*a* 5.48 ** *b* 9.85, *c* 12.28, β 99.2	*a* 5.53 *b* 9.91, *c* 12.59, β 99.5	*a* 5.43 *b* 9.98, *c* 12.27, β 99.87
Calculated density of the crystal, kg m^{-3}	3920	4018	5570	5815

*Refinement of Ref. 110.

**According to Ref. 111, the lattice parameters of RhF_5 are: $a = 5.5173$, $b = 9.9177$, $c = 12.3376$ Å; $\beta = 100.42°$; density of the crystals 3950 kg m^{-3}.

The vapour pressure (p, mmHg) is described by the equations:

for RuF_5 (Ref. 94) $\lg p = 9.54 - 3329/T$ ($363.15 \leqslant T \leqslant 433.15$ K),
for OsF_5 (Ref. 106) $\lg p = 9.75 - 3429/T$ ($343.15 \leqslant T \leqslant 453.15$K).

The mass-spectrometric study of the composition of the saturated vapour of the platinum metal pentafluorides has shown[104,113,114] that close to room temperature, RuF_5, RhF_5, and IrF_5 form dimers, trimers, and tetramers, and OsF_5 and PtF_5 for dimers and trimers.

The vibrational frequencies of the two possible structural forms of the platinum metal pentafluorides, and the thermodynamic functions in the temperature range 298–3200 K, have been calculated[115]. The infrared spectrum of solid RuF_5, recorded in the range 400–1000 cm^{-1},[116] shows bands at 525, 645, 670, 715, and 750 cm^{-1}.

The chemical properties of the platinum metal pentafluorides have been less extensively studied. Ruthenium pentafluoride can be kept for a long time in nickel and quartz containers at room temperature, but begins to react slowly with Pyrex even at 370 K. When dissolved in water, RuF_5 is hydrolysed instantly to give a brownish–black solution and a precipitate of $RuO_2.nH_2O$; disproportionation also leads to the partial liberation of volatile RuO_4.[94] OsF_5 behaves similarly, forming $OsO_2.nH_2O$ and OsO_4 on hydrolysis[67]. Rhodium pentafluoride also reacts vigorously with H_2O, but the hydrolysis products could not be identified[97]. When PtF_5 is dissolved in water, PtO_2 is formed (25% of the total Pt), and the solution contains the rest of the platinum as the PtF_6^{2-} ion; in addition, O_2 is liberated[107].

The reaction of RuF_5 with CO in a flow system at 470 K gives a non-volatile solid product with the composition $Ru(CO)F_{3.5}$.[117] Iridium pentafluoride at 530–550 K reacts with CO to give a product with the composition $Ir(CO)_{2-3}F_2$.[118]

The reactions of molten XeF_2 with osmium and ruthenium pentafluorides give coloured crystalline adducts with the composition $XeF_2.OsF_5$, $XeF_2.RuF_5$, and $XeF_2.2RuF_5$.[119] The adducts $2XeF_2.MF_5$ and $XeF_2.MF_5$ (M = Ru, Os, Ir, Pt) and also $XeF_2.2MF_5$ (M = Ru, Ir, Pt) were obtained by the reaction of the corresponding platinum metal pentafluorides with a solution of XeF_2 in BrF_5.[120] Iridium pentafluoride forms adducts $2XeF_6.IrF_5$ and $XeF_6.IrF_5$.[121] The reaction of an equimolar mixture of Xe and PtF_5 with fluorine under pressure at a temperature of 450–490 K gave crystals of $XeF_5^+PtF_6^-$ and $Xe_2F_{11}^+PtF_6^-$.[109,122] A study of the crystal structure of these compounds[116,119–123] confirmed that they are ionic. The reaction of RuF_5 with KrF_2 in anhydrous HF also gives relatively stable adducts, as confirmed by the Raman spectra[124].

Osmium[106] and platinum[107] pentafluorides when heated disproportionate according to the equation

$$2MF_5 \rightarrow MF_4 + MF_6.$$

Platinum pentafluoride shows the properties of a relatively strong Lewis acid; it forms $NOPtF_6$ with NOF,[72] $2BrF_3.PtF_6$ with BrF_3, $2SeF_4.PtF_4$ with SeF_4, and $IF_5.PtF_5$ with IF_5.[107]

Comparison of the platinum metal pentafluorides with other known rare metal pentafluorides indicates that their properties are closer to those of the pentafluorides of molybdenum, niobium, and tantalum. The structural unit of all these pentafluorides is the tetramer $(MF_5)_4$, with bridging fluorine atoms in the *cis*-position and octahedral coordination of the metal. The average $M-F_{terminal}$ and $M-F_{bridging}$ distances in the tetramers of the pentafluorides of the platinum metals and molybdenum, niobium, or tantalum are similar; the values for the latter are 1.77 Å and 2.06 Å. These compounds are also polymerised in the gaseous state, and the platinum metal pentafluorides are also polymerised in the liquid state. The melting points and boiling points of MoF_5, NbF_5, and TaF_5 (340 and 487, 353.15 and 508, and 370.1 and 502 K respectively) and enthalpies of volatilisation (47.4, 51.0, and 54.3 kJ $mole^{-1}$) [16] are close to those for the platinum metal pentafluorides.

3. Tetrafluorides

All the platinum metals form tetrafluorides. The sandy-yellow RuF_4 is obtained by the reaction of an excess of RuF_5 with iodine in IF_5 [125] or by reducing RuF_5 with hydrogen in anhydrous HF.[75] The purple–red RhF_4 is obtained by the action of liquid BrF_3 on $RhBr_3$ or $RhCl_3$ with subsequent thermal decomposition of the adducts[126]. Red–brown PdF_4 has been synthesised by fluorinating PdF_3 with fluorine at a pressure of 7 atom and a temperature of 570–620 K.[127] Yellow–brown OsF_4 is formed, together with OsF_5, by the reaction of OsF_6 with $W(CO)_6$, and can be separated from the more volatile OsF_5 by vacuum distillation[67]. Osmium and iridium tetrafluorides are obtained by reducing their pentafluorides with hydrogen or powdered Si in anhydrous HF.[100,101] The rate of the process is increased by using Pt gauze or ultraviolet irradiation.

The reduction of IrF_6 using an electrically heated tungsten or iridium spiral in a Pyrex reaction vessel with walls cooled to 230 K gave red–brown IrF_4.[128] IrF_4 has also been synthesised by the reaction of IrF_6 with PF_3 in anhydrous HF.[74] Other reports of the synthesis of IrF_4 [25,129] have been refuted[68].

The action of an excess of BrF_3 on $PtCl_4$ or $PtBr_4$ at room temperature gives the adduct $(BrF_3)_2PtF_4$, which when heated in a vacuum to 450–470 K gives pale-brown PtF_4.[126] In this case, however, BrF_3 is not completely removed even by heating to 570 K, and further increase in temperature leads to decomposition of PtF_4. BrF_3 has been removed completely by treatment with fluorine at a low temperature[107]. The same paper described a method for preparing PtF_4 by heating $PtCl_2$ to 470–520 K in a stream of HF diluted with nitrogen. Platinum tetrafluoride is obtained by fluorinating spongy Pt and $PtCl_2$ with fluorine in a quartz apparatus at temperatures below 470 K.[103] The pure tetrafluoride is obtained by heating a $PtF_6 + PtF_x$ ($4 < x < 5$) mixture at 470 K for several hours and then removing the excess of fluorine in a vacuum[28].

There is almost no published information on the physical properties of the platinum metal tetrafluorides. RuF_4 does not melt up to 550 K.[125] OsF_4 melts at 403 K.[67] Iridium tetrafluoride begins to sublime at 450 K, and decompose at 670 K; the mass spectrum of IrF_4 showed that it is not associated in the vapour[128]. A thermodynamic study of gaseous PtF_4, formed by introducing fluorine into the effusion compartment of a mass spectrometer at 518–960 K, showed that for the reaction $Pt(solid) + 2F_2(gas) \rightleftharpoons PtF_4(gas)$ at 793 K, the change in the Gibbs free energy is −158 kJ $mole^{-1}$, and the enthalpy of formation of gaseous PtF_4 at 793 K is −214 kJ $mole^{-1}$.[130] A similar method in the temperature range 860–980 K using exchange reactions in the MnF_2–MnF_3–Pt system gave the enthalpy of formation of gaseous PtF_4. At 298 K, ΔH^0[form. $PtF_4(gas)$] = −410 ± 40 kJ $mole^{-1}$, and the dissociation energy $D^0(PtF_2-F_2)$ = 330 ± 40 kJ $mole^{-1}$.[131] The magnetic moments of RuF_4 [125] and RhF_4 [132] at 291 K are 3.04 B.M. and 1.1 B.M. respectively; PdF_4 and PtF_4 are diamagnetic[127,107].

An X-ray diffraction study of PdF_4, IrF_4, and PtF_4 [133] showed that they form monoclinic crystals, $Z = 8$, space group $Fdd2$ with lattice parameters $a = 9.35$, $b = 9.25$, $c = 5.84$ Å, $\beta = 90.7°$; $a = 9.61$, $b = 9.28$, $c = 5.71$ Å, $\beta = 92.0°$; $a = 9.64$, $b = 9.25$, $c = 5.67$ Å, $\beta = 92.7°$ respectively. A later and more accurate neutron diffraction study of PdF_4 [134] indicated that PdF_4 forms orthorhombic crystals ($Z = 8$, space group $Fdd2$, lattice parameters $a = 9.339$, $b = 9.240$, $c = 5.828$ Å) and is isostructural with IrF_4, previously studied by X-ray diffraction[133,135]. The Pd atom shows octahedral coordination; four F atoms are bridging (Pd–F distances 1.91 Å and 2.00 Å), and two are terminal, with the *cis*-arrangement (Pd–F distance 1.94 Å). The bridging angle PdFPd (134.0°) is close to the ideal value of 135° required for hexagonal closest packing of the octahedra. The ^{19}F NMR spectra of platinum and palladium tetrafluorides confirmed[136] that they show only octahedral coordination with non-equivalent F atoms. The crystal structure of RhF_4 has been studied[137]. The lattice parameters are $a = 9.71$, $b = 9.05$, $c = 5.63$ Å, $Z = 8$. According to Ref.133, RhF_4 is not isomorphous with PdF_4, PtF_4, and IrF_4, and the structure of RuF_4 is different from those of all the above tetrafluorides. The calculated densities of PdF_4 and PtF_4 crystals[16] are 4790 kg m^{-3} and 7070 kg m^{-3} respectively, and that of IrF_4 [133] is 7050 kg m^{-3}.

The vibrational frequencies of the platinum metal tetrafluorides have been calculated assuming T_d symmetry and M–F distances equal to those in the hexafluorides[115]. The experimentally determined vibrational frequencies in the infrared spectra of OsF_4 and IrF_4 are 719, 702, 660, 532 cm^{-1} and 691, 688, 545 cm^{-1} respectively[101]. According to Ref.74, the infrared spectrum of IrF_4 show bands at 685, 660, 609, 558, and 460 cm^{-1}.

The tetrafluorides of ruthenium[125], rhodium[126], and palladium[127] react vigorously with water to give $RuO_2.nH_2O$ and $RhO_2.nH_2O$ (the hydrolysis products of PdF_4 have not been identified). Osmium tetrafluoride dissolves in water to give a transparent yellow solution[67], and PtF_4 is hydrolysed slowly

to give a precipitate of PtO_2 and a solution containing the PtF_6^{2-} ion[107].

Rhodium tetrafluoride oxidises HCl to Cl_2; it does not react with ether or CCl_4 at room temperature[126]. Heating RhF_4 with an excess of SeF_4 gives $(RhF_4)_2SeF_4$.[138] The reaction of RhF_4 with CO gives $Rh(CO)_2F_3$, and the action of CO under pressure on PtF_4 gives the compound $Pt(CO)_2F_8$.[139]

Platinum tetrafluoride is reduced to the metal by hydrogen at 370 K, reacts with BrF_3 to give $(BrF_3)_2PtF_4$, and does not react with IF_5 and is insoluble in it. Evaporation of a solution of PtF_4 in SeF_4 in a vacuum gives $(SeF_3)_2PtF_6$.[107] Platinum tetrafluoride in acetone reacts at 273 K with a small quantity of H_2O, forming $H_2Pt(OH)_4F_2$, and with CH_3OH in acetone it forms the substance $PtF_2(OCH_3)_2$, which is explosive at 360 K.[140] Liquid XeF_2 at 410–420 K oxidised PtF_4, forming $Xe_2F_3PtF_6$.[141] A DTA study of the BrF_3–PtF_4 system detected the incongruently melting compounds $2BrF_3.PtF_4$ and $7BrF_3.PtF_4$.[142]

Palladium tetrafluoride is readily reduced to PdF_3, and decomposes to give the same compound when heated in a vacuum[127]. Compounds of different composition are formed by the reaction of PdF_4 with XeF_6 and XeF_2.[133,141]

4. Trifluorides

Brown RuF_3 has been obtained by reducing ruthenium pentafluoride with an excess of iodine at 420 K or with sulphur at 470 K.[143] Red RhF_3, contaminated by metallic rhodium, was first obtained by fluorinating rhodium or $RhCl_3$ with fluorine at a dull red heat (below 770 K).[144,145] Pure RhF_3 was synthesised by the reaction of RhI_3 with fluorine at 670–770 K.[146] Iridium trifluoride (black) was obtained by reducing IrF_6 with metallic iridium[146].

The physical characteristics of the platinum metal trifluorides have not been studied. An X-ray diffraction study of RuF_3, RhF_3, and IrF_3 [146] showed that they form orthorhombic crystals with the VF_3 structure, space group $R\bar{3}c$, $Z = 2$. The orthorhombic cell corresponds to a hexagonal pseudo-cell. The structural characteristics and densities of the crystalline platinum metal trifluorides are given in Table 8.

Table 8. Structural characteristics and densities of the crystals of the platinum metal trifluorides[146].

Trifluoride	Lattice parameters, Å, and angle F–M–F, °			Calculated density of the crystals, kg m^{-3}
	bimolecular rhombohedral cell	hexagonal cell, $Z = 6$	monomolecular rhombohedral cell	
RuF_3	a 5.408±0.001; α 54.67±0.01	a 4.967, c 13.756	a 3.672, α 85.13	5350 *
RhF_3	a 5.330±0.001; α 54.42±0.01	a 4.874, c 13.579	a 3.611, α 84.89	5690 *
IrF_3	a 5.418±0.002; α 54.13±0.03	a 4.940, c 13.819	a 3.666, α 84.72	8520

*Calculated in Ref. 12.

There are almost no published data on the chemical properties of the platinum metal trifluorides. RuF_3 is hydrolysed in water, but insoluble in it; it is also insoluble in dilute acids or alkalis[143]. When heated in a stream of fluorine, RuF_3 gives RuF_5.[147] Rhodium trifluoride is not hygroscopic, insoluble in water, and almost unaffected by hot concentrated HCl, HNO_3, HF (40%), or NaOH. When heated, it is reduced exothermally by H_2, NH_3, SO_2, P, Si, Fe, Al, Na, and Mg.[144,145]

Palladium trifluoride has been obtained by dissolving $PdBr_2$ or PdI_2 in bromine trifluoride, followed by thermal decomposition in a vacuum of the resulting adduct $PdF_3.BrF_3$,[126] or by fluorinating metallic palladium and its halides with fluorine[146]. Its magnetic properties were explained by assuming that this substance does not contain Pd^{III} but is $Pd^{2+}Pd^{4+}F_6$, whose effective magnetic moment (2.88 B.M.) corresponds to the moment of the d^8 configuration of Pd^{2+}.[127]

Measurements of the enthalpy of the reaction $PdPdF_6$(solid) + $3PF_3$(gas) = $3PF_5$(gas) + 2Pd in a bomb calorimeter gave ΔH^0(form.$PdPdF_6$(solid) 298.15 K) = −967.4 ± 7.3 kJ mole^{-1}.[148]

$PdPdF_6$ forms rhombohedral crystals, space group $R\bar{3}c$, $Z = 2$, with lattice parameters: $a = 5.5234 \pm 0.0005$ Å, $\alpha = 53.925 \pm 0.005°$. The calculated and measured densities of PdF_3 are 5315 kg m^{-3} and 5060 kg m^{-3} respectively. The structure of $PdPdF_6$ is related to the $LiSbF_6$ structure, and contains Pd^{II} and Pd^{IV} atoms surrounded octahedrally by F atoms (Pd^{II}–F distance 2.17 Å, Pd^{IV}–F distance 1.90 Å).[146,149]

A study of the influence of high pressure (up to 9×10^4 atm) on the properties of $PdPdF_6$ showed[150,151] that with increase in pressure there is a marked increase in the electrical conductivity, probably due to the electron transfer $Pd^{2+} + Pd^{4+} \rightarrow Pd^{3+}$. At 410–420 K, $PdPdF_6$ is oxidised by liquid XeF_2 to $XePdF_6$.[141]

A study of the reaction of Pt powder with fluorine at different temperatures established[152] that at 670–720 K the product is the fluoride $Pt^{2+}Pt^{4+}F_6$, which at 570–620 K is present in a mixture with PtF_4. The yellow hygroscopic $PtPtF_6$ powder decomposes to the elements at 460 K. The rhombohedral lattice parameters have been determined by X-ray diffraction: $a = 5.56$ Å, $\alpha = 53.85°$, space group $R\bar{3}$, density of the crystals (calculated) 7977 kg m^{-3}, $LiSbF_6$ structure.

5. Dichlorides

Only palladium difluoride is known and has been reliably characterised. Heating $BrF_3.PdF_3$ with SeF_4 gives $(SeF_3)_2.PdF_6$, which at 430 K decomposes rapidly to pale-violet PdF_2.[153,154] It can also be obtained by the direct reduction of $PdPdF_6$ with boiling SeF_4.[154] Fluorination of Pd powder gives a mixture of Pd and PdF_2, further treatment of which with fluorine at 770–1020 K gives PdF_2.[155]

Palladium difluoride crystallises with the tetragonal rutile structure, space group $P4_2/mnm$, $a = 4.956$ Å, $c = 3.389$ Å, $Z = 2$,[153,156] density of the crystals (calculated) 5760 kg m^{-3}.[16] At a pressure of 6×10^4 atm and 720 K in an argon atmosphere, the product is the violet–brown cubic form of PdF_2 (space group $Pa3$, $CdPdF_4$ structure, $a = 5.32$ Å), which is metastable at normal pressure[157]. PdF_2 obtained by the solid-phase reaction of a stoichiometric mixture of $PdPdF_6$ and dispersed Pd in an evacuated Pd tube at 870 K and a pressure of up to 9×10^4 atm undergoes a polymorphic transformation to give a phase isostructural with fluorite[151,158]. The electrical conductivity increases sharply (by a factor of 10^5).

Palladium difluoride is rapidly hydrolysed in moist air, and is decomposed exothermally by water[153].

ΔH^0[form. 198.15 K, PtF_2(gas)] = −80 ± 42 kJ mole^{-1}, and the dissociation energy $D^0(Pt–F_2)$ = 644 ± 42 kJ mole^{-1}.[130,131]

III. PLATINUM METAL OXIDE FLUORIDES

The platinum metals can form various oxide fluorides (Table 9), but these are known for only three metals—OsO_3F_2, OsO_2F_3, $OsOF_5$, $OsOF_4$, $RuOF_4$, and $PtOF_3$. The hypothetical $PtOF_4$ [101] was found to be O_2PtF_6.[80]

Orange OsO_3F_2 powder was first obtained by the reaction of Os with a mixture of F_2 and O_2 (2 : 1).[159] OsO_3F_2 has also been synthesised by heating a mixture of F_2 and OsO_4 (2 : 1, 570 K, 50 h).[70] OsO_3F_2 melts at 443–446 K.[79,159] The magnetic susceptibility and mass spectra of OsO_3F_2 have been recorded[160]. The principal vibrational frequencies in the infrared and Raman spectra of matrix-isolated OsO_3F_2 have been determined and assigned[161]: $\nu_1(A_1') = 946.5$, $\nu_2(E') = 928.5$, $\nu_3(A_2'') = 646$, $\nu_4(A_1') = 619$, $\nu_5(E'') = 348$, $\nu_6(E') = 316.5$, $\nu_7(A_2'') = 258$, and $\nu_8(E') = 206$ cm^{-1}. OsO_3F_2 has D_{3h} symmetry. The force constants of OsO_3F_2 have been calculated in a Urey–Bradley force field[162]. The thermodynamic functions of gaseous OsO_3F_2 in the temperature range 298–6000 K have been calculated in the rigid rotator–harmonic oscillator approximation[163]. The values of the heat capacity (C_p^0) and S^0, calculated at 298.15 K, are 96.631 J mole^{-1} K^{-1} and 327.18 J mole^{-1} K^{-1} respectively.

Table 9. Platinum metal oxide fluorides.

Oxidation state of the metal			
M (VIII)	M (VII)	M (VI)	M (V)
MO_3F_2	(MO_3F)	(MO_2F_2)	(MO_2F)
(MO_2F_4)	MO_2F_3	MOF_4	MOF_3
—	MOF_5	—	—

Note. Compounds whose existence is assumed are given in bracket.

Of the chemical properties of OsO_3F_2 it is known that it does not decompose on Pyrex, but is rapidly hydrolysed in the presence of moisture to OsO_4 and HF.[159]

Yellow-green OsO_2F_3 has been synthesised from an equimolar mixture of OsO_4 and OsF_6 (420 K, 17 h), and also from $OsOF_4$ and OsO_3F_2 (370 K, 12 h).[70,160] The magnetic susceptibility, mass spectrum, and EPR and Raman spectra of OsO_2F_3 have been recorded, and the vibrational frequencies assigned[160]. Solid OsO_2F_3 is polymeric, and probably has a structure containing tetrameric groups in which Os atoms with formal charges of 6+ and 8+ are joined by F-bridges.

OsO_2F_3 is sensitive to moisture, and is comparatively stable at room temperature, but it disproportionates at 330 to 350 K to give a mixture of $OsOF_4$ and OsO_3F_2; above 380 K, the equilibrium mixture also contains OsF_6 and OsO_4.[160]

The most fully studied platinum metal oxide fluoride is the emerald-green osmium oxide pentafluoride. It was obtained by heating Os in a stream of a mixture of O_2 and F_2 (1 : 2 by volume), and also by passing F_2, diluted with N_2, over OsO_2 and by heating Os in a Monel bomb with a mixture of O_2 and F_2 (1.0 : 2.5) at 570 K.[164,165] In all cases the product was a mixture of $OsOF_5$ (yield ~ 50%) and OsF_6, from which the more volatile OsF_6 was removed by vacuum distillation. $OsOF_5$ was obtained in more than 90% yield by the action of a slight excess of F_2 on anhydrous OsO_2 at 520 K.[165] $OsOF_5$ has also been synthesised by treating Os, placed in the atomic fluorine generation zone, with a mixture of O_2 and F_2 (1 : 3 by volume).[166]

The physical properties of $OsOF_5$ are given in Table 10.

The X-ray diffraction study of $OsOF_5$ [164,165,168] has shown that below 306 K it has the orthorhombic YF_3 structure, space group *Pnma*, $Z = 4$, density of the crystals (calculated) 4820 kg m^{-3}, lattice parameters $a = 9.540$, $b = 8.669$, $c = 5.019$ Å; above 306 K it is converted into a cubic form, $Z = 2$, $a = 6.14$ Å. Comparison of the structural data for $OsOF_5$ and the platinum metal hexafluorides (see Table 2) shows that they are isostructural. The fact that all the bonds formed by Os with neighbouring atoms in $OsOF_5$ are shorter than the Os–F bonds in the OsF_6 molecule (1.831 Å) is apparently due to the greater polarisation by Os in the first case[168].

Table 10. Physical properties of $OsOF_5$.[165]

Property	Value
M.p., K	332.35
B.p., K	373.75
$T_{p.t.}$, K	305.65
ΔH^0_{fusion}, kJ mole^{-1}	6.8
$\Delta H^0_{volatilisation}$, kJ mole^{-1}	36.6
$\Delta H^0_{sublimation}$, kJ mole^{-1}	43.4
ΔS^0_{fusion}, J mole^{-1} K^{-1}	22.1
$\Delta S^0_{volatilisation}$, J mole^{-1} K^{-1}	98
C_p^0 for the gas at 298.15 K, J mole^{-1} K^{-1}	118 *
S^0 for the gas at 298.15 K, J mole^{-1} K^{-1}	356 *
Magnetic moment μ, B.M.	1.47

*According to Ref. 167.

The $OsOF_5$ molecule has a slightly distorted octahedral structure with interatomic distances $r(Os–O) = 1.74$, $r(Os–F_{ax}) = 1.76$, and $r(Os–F_{eq}) = 1.80$ Å. The thermodynamic properties of $OsOF_5$ are also close to those of the platinum metal hexafluorides (Tables 1 and 10).

The vapour pressure (p, mmHg) of $OsOF_5$ is given by the equations[165]:

$$\lg p = 9.064 - 2266/T \quad (305 \leqslant T \leqslant 332\text{K}),$$
$$\lg p = 7.994 - 1911/T \quad (332 \leqslant T \leqslant 378\text{K}).$$

The infrared, Raman, and ^{19}F NMR spectra indicate that the $OsOF_5$ molecule belongs to the symmetry group C_{4v} [165,166,169,170]. The frequencies required for this configuration have been determined for gaseous $OsOF_5$: 962.6, 716.4, 644, 280.5, 645, 210, 332, 700.6, 263, 367, and 167 cm^{-1}.[170] The presence in the infrared spectrum of solid $OsOF_5$ of a band at 530 cm^{-1}, characteristic of the vibration of the Os–F–Os bridging bond, indicates that $OsOF_5$ is polymerised in the solid state[166]. The ^{19}F NMR spectrum indicates that the non-bonded *d* electrons are localised in the equatorial plane of the molecule[169].

$OsOF_5$ is stable in dry air, but decomposes in the presence of moisture to give OsO_4.[164] The oxidising properties of $OsOF_5$ are similar to those of OsF_6, but the former is a much weaker F^- acceptor[59].

Osmium oxide tetrafluoride was obtained by reducing $OsOF_5$ on an electrically heated tungsten wire[171] or by the reaction of OsF_6 with OsO_4 (2.5 : 1.0) at 450 K.[70] A general method for the synthesis of transition metal oxide fluorides, including $OsOF_4$, has been described, based on the exchange reaction of the corresponding hexafluorides with finely divided B_2O_3. A convenient method for synthesising $OsOF_4$ involves the hydrolysis of OsF_6 in hydrogen fluoride with an accurately measured quantity of H_2O.[71] $OsOF_4$ can be obtained by reducing $OsOF_5$ with finely dispersed Si powder in anhydrous HF.[166] The last two methods of obtaining $OsOF_4$ are preferred, since they do not require additional operations to remove the OsF_5 which usually accompanies it.

The orthorhombic lattice parameters of $OsOF_4$ [171] are $a = 5.56$, $b = 9.56$, $c = 12.83$ Å, the density of the crystals (measured) 5500 kg m^{-3}, $Z = 8$, space group $P2_122_1$.

The infrared spectrum of crystalline $OsOF_4$ has been studied[77,166]. According to Ref.166, the spectrum contains bands at 1010, 958, 707, 672, 649, and 535 cm^{-1}. The 1010 cm^{-1} band was assigned to the Os=O stretch, and the bands at 600–750 cm^{-1} to bridging Os–F–Os stretches. These bands in the range 500–600 cm^{-1} are characteristic of other transition metal oxide tetrafluorides and oxide pentafluorides[172], and indicate that they have a polymeric structure, in agreement with X-ray diffraction[171] and Raman spectroscopic[160] data. An electron diffraction study of $OsOF_4$ [166] showed best agreement with an equilibrium configuration with symmetry C_{4v} (a tetragonal pyramid with the oxygen atom in the axial position), previously established for $ReOF_4$ and WOF_4.[173] The existence of the four-fold axis in the $OsOF_4$ molecule was confirmed by photoelectron spectroscopy[174]. Analysis of the photoelectron spectra of the oxide tetrafluorides of tungsten, rhenium, and osmium shows an increase in the ionic character of the M–F bond in this order, and indicates that the multiplicity of the M–O bond must be close to 3, since the covalent bonding involves not 2 but 3 electron pairs, $(5a_1)^2$, $(5e)^4$. The last conclusion is confirmed by the results of electron diffraction studies[166] [r(Os–O) = 1.625, r(Os–F) = 1.835, r(O–F) = 2.825, r(F–F) = 2.466 Å], from which it follows that the Os–O bond in $OsOF_4$ is 0.115 Å shorter than the Os–O bond in $OsOF_5$. $OsOF_4$ is extremely sensitive to moisture, and dissolves in water and alkali solutions to give transparent yellow solutions with an odour of ozone (OsO_4 is apparently liberated)[77]. The fluorination of $OsOF_4$ at 450 K gives $OsOF_5$,[70] and heating an equimolar mixture of $OsOF_4$ and OsO_3F_2 at 370 K gives OsO_2F_3.[160]

The preparation of $RuOF_4$ by the reaction of metallic Ru with a mixture of BrF_3 and Br_2 (1 : 1) at room temperature has been described[94]. The source of oxygen was the wall of the reaction vessel. When the reaction was complete, BrF_3 was removed in a vacuum at 390 K, and the residue was heated in a sealed evacuated glass tube for 3–5 weeks at 310 K. According to Ref.94, $RuOF_4$ is a colourless substance, coloured pale green by impurities, which melts at 388 K, boils at 457 K, and has a heat of volatilisation of 50 kJ $mole^{-1}$. The vapour pressure (p, mmHg) is given by the equations

$$\text{for } RuOF_4\ [94]\ \lg p = 9.22 - 2857/T\ (293 \leqslant T \leqslant 373\text{K})$$
$$\lg p = 8.60 - 2616/T\ (393 \leqslant T \leqslant 433\text{K}).$$

Japanese workers who studied the behaviour of ruthenium during the sublimation of the fluorides to solve the problems of processing irradiated nuclear fuel[175–178] consider that the data in Ref.94 are erroneous, for the following reasons: 1) a stoichiometric reaction component ratio with respect to oxygen was not observed; 2) the presence of oxygen in the final products was not confirmed, and 3) the components of the gas phase were not analysed before the vapour pressure was measured. A study of the kinetics of the reaction of RuO_2 with fluorine in a flow reactor in the range 523–773 K at a fluorine partial pressure of 150 mmHg [175] showed that at temperatures above 670 K, RuO_2 is completely converted to $RuOF_4$, whose formation was confirmed by chemical analysis and from the mass and infrared spectra. The thermal decomposition of $RuOF_4$ was studied[176] by gas chromatography at 290–670 K, combined with chemical analysis and an infrared spectroscopic study of the solid residue and measurement of the vapour pressure by a transpiration method. Solid $RuOF_4$ decomposes to give O_2 and solid RuF_4, and the process takes place even at 293 K. With increase in temperature to 340 K, the decomposition rate increases to a maximum, and with further increase in temperature it decreases, although a small quantity of O_2 is liberated even at 670 K.

The authors cited[176] consider that the static method of measuring the vapour pressure of $RuOF_4$, used in Ref.94, is not suitable, because of errors associated with the liberation of oxygen. Moreover, at temperatures above 340 K, the RuF_4 formed prevents the normal volatilisation of $RuOF_4$. According to Ref.176, the equilibrium vapour pressure of $RuOF_4$ in the range 273–343 K is described by the equation $\lg p$ (mmHg) = 8.48 – 2740/T. It is pointed out that $RuOF_4$ vapour is stable, and that the instability of solid $RuOF_4$ is apparently related to the fact that the Ru^{VI} corresponds to an excited state. The bands at 1040 cm^{-1} and 720 cm^{-1} in the infrared spectrum of gaseous $RuOF_4$ were assigned to the Ru=O and Ru–F vibrations respectively. The spectrum of solid $RuOF_4$ does not show a band at 1040 cm^{-1}, but shows bands at 720, 630, and 520 cm^{-1}. The first of these was assigned to Ru–F stretches, the second to single bond Ru–O stretches, and the last to bridging Ru–F–Ru vibrations.

The fluorination of Ru with a mixture of F_2 and O_2 at 570–670 K gives RuF_5 (76–84%), $RuOF_4$ (16–24%), and small quantities of RuO_4.[178] These results differ from earlier data[19,179], and require confirmation.

Mass spectrometry, infrared spectroscopy, DTA, and TGA have established that at room temperature, a series of reactions involving the hydrolysis of $RuOF_4$, RuF_4, and RuF_5 followed by treatment of the hydrolysis products (mainly ruthenium hydroxides) with gaseous fluorine is accompanied by their almost complete conversion into RuO_4:[177]

$$Ru(OH)_4 \cdot n H_2O + (2+n) F_2 \rightarrow RuO_4 + 2(2+n) HF + n/2O_2.$$

Platinum oxide fluoride has been obtained by fluorinating PtO_2 at 470 K; it is nonvolatile, is slowly hydrolysed in moist air, and its behaviour towards water is the same as that of PtF_4.[107]

IV. DIOXYGENYL COMPOUNDS OF THE PLATINUM METALS

Dioxygenyl hexafluoroplatinate O_2PtF_6 was first obtained[103] by fluorinating spongy platinum or $PtCl_2$ at 620 K in a quartz apparatus, but was erroneously assumed to be $PtOF_4$. The true composition of the compound was determined soon afterwards[80].

Methods for preparing O_2PtF_6 have been described[81]. They include fluorination in quartz, the action of a mixture of F_2 and O_2 on Pt at 720 K, the reaction of OF_2 with Pt above 670 K, and the reaction of equimolar quantities of PtF_6 and O_2 at room temperature. The compounds O_2RuF_6 and O_2RhF_6 were obtained by heating the corresponding powdered metal with a mixture of F_2 and O_2 (3 : 1 and 4 : 1) for a long time (up to 60 h) at 570–770 K.[180] The fluorination of oxides of Ru, Rh, and Pt by atomic fluorine also gives dioxygenyl compounds[30]. According to Ref.21, the reaction of PdF_6 with O_2 gives an orange compound, apparently O_2PdF_6.

An X-ray diffraction study of O_2PtF_6 [80,81] showed that it forms cubic or orthorhombic crystals. The high-temperature cubic form, obtained by the reaction of OF_2 with Pt at a temperature above 673 K, has lattice parameter a = 10.032 ± 0.002 Å, space group $Ia3$, Z = 8, and calculated and measured densities 4480 kg m^{-3} and 4200 kg m^{-3} respectively. For the low-temperature orthorhombic form, obtained by the reaction of PtF_6 with O_2 in liquid N_2, a = 4.96 Å, α = 97.5°, density 4725 kg m^{-3}. For the cubic O_2RuF_6 lattice, a = 10.004 Å, and for rhombohedral O_2RhF_6, a = 5.05 Å, α = 97°.[180]

The chemical properties and infrared and ultraviolet absorption spectra indicate that dioxygenyl hexafluoroplatinate has an ionic structure. The lattice energy of $O_2^+PtF_6^-$ is about 500 kJ $mole^{-1}$. The composition of the compounds O_2MF_6 (M = Ru, Rh, Pt) was confirmed by the Raman and mass spectra[180,181].

O_2PtF_6 reacts vigorously with H_2O to give a pale-yellow solution containing PtF_6^{2-} ions and a black solid residue containing metallic platinum, with the liberation of oxygen and a gas with the odour of ozone[81]. The hydrolysis of O_2PtF_6 and O_2RuF_6 in 40% NaOH takes place according to the equation[182]:

$$O_2MF_6 + 2OH^- \rightarrow 1.5O_2 + MF_6^{3-} + H_2O.$$

O_2PtF_6 reacts with BrF_3, SeF_4, IF_5, and ClF_3 at room temperature to form various adducts[81]. The reaction of O_2RuF_6 at 298 K and of O_2RhF_6 and O_2PtF_6 at 379 K with an excess of NOF gives the nitrosyl compounds $NORuF_6$, $(NO)_2RhF_6$, and $(NO)_2PtF_6$.[72]

V. SUMMARY

The chemistry of the platinum metal fluorides has developed rapidly in the last 25 years. Discoveries such as the synthesis of O_2PtF_6 and $XePtF_6$ have been among the most significant in inorganic chemistry in recent decades. Nevertheless, the physicochemical properties and methods of synthesis of the platinum metal fluorides examined in the present review show that there are many "blank spots" in this field.

The most important task is still the development of simple and reliable methods for preparing platinum metal fluorides of sufficient purity. Existing methods are complicated by the fact that the isolation of individual substances requires a large number of additional operations to separate the compounds formed. High demands are also made of the purity of the starting materials, since for example traces of oxygen in the metal or fluorine leads to contamination of the hexafluorides with oxide fluorides[37]. Here, promising methods involve the use of solutions of KrF_2 and XeF_2 in anhydrous hydrogen fluoride, the use of atomic fluorine[29,30,96], and the use of selective sorption and selective reduction.

The lower fluorides of the platinum metals have been very little studied, and there are practically no data on their structure and chemical and thermal properties.

The most important problems in the field of platinum metal fluorides include the determination of the thermodynamic parameters, the lack of which makes it difficult to solve problems associated with the application of the platinum metal fluorides.

From the practical viewpoint, the platinum metal fluorides are of interest because of their high volatility and the consequent possibility of their use in processes of fluoride metallurgy[183,184]. This technology in principle has all the advantages of non-aqueous methods, and can simplify the existing multi-stage schemes for separating and purifying the platinum metals. The demand and the price of the platinum metals continue to increase[185], so that a change to short technological schemes and the associated marked decrease in losses are undoubtedly justified.

Fluorination may also prove extremely promising for the analysis of the platinum metals, which are difficult to dissolve quantitatively.

The present review has not examined the large number of complex fluorides of the platinum metals, which are also interesting materials for scientific study and which may find practical application, for example for the separation and purification of the platinum metals.

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Metal-containing Monomers: Advances in Polymerisation and Copolymerisation

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The main advances in and problems of polymerisation, copolymerisation, as well as graft polymerisation of metal-containing monomers (MCM) are analysed. These are classified in terms of the type of bond between the metal and the organic component of the molecule into three principal groups, namely MCM with σ-, $n\nu$-, and π-bonded metal, are analysed. Attention is concentrated on the influence of the nature of the metal (both transition and non-transition) on the polymerisation process and on the properties of the products. A systematic account is given of the principal data for the polycondensation of metal-containing compounds. The applications of the metal polymer synthesised are considered.
The bibliography includes 215 references.

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I. INTRODUCTION

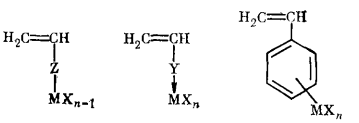
Metal-containing polymers have found extensive applications in recent years in the preparation of various coatings with special properties, catalysts, as thermoplastic constructional materials, etc. At the same time clearly inadequate attention has been devoted to problems of the synthesis of metal-containing monomers (MCM) and the characteristic features of their polymerisation, copolymerisation, and graft polymerisation. Only ferrocene and certain other metallocene compounds are perhaps exceptions in this respect[1]. Although the first publications of the radical polymerisation of vinylferrocene date back to as early as 1955,[2] subsequently attention was concentrated on coordination polymers[3]; studies on the polymerisation of MCM developed more slowly, primarily owing to the difficulty of the synthesis of such MCM and also the specific features of their polymerisation and copolymerisation. The presence of metal atoms in molecules of this class leads to the formation of coordinate bonds in the polymerisation process and a redistribution of electron density at the growing centre, which has a significant influence on the polymerisation mechanism.

In recent years there has been an appreciable growth of interest in the polymerisation of MCM. Three international specialist symposia, devoted to the polymerisation of MCM and the study of the properties of organometallic polymers, have already been held in the USA.[4,5] Much attention has been devoted to these problems in the USSR in the investigations of Nesmeyanov and co-workers[6], Korshak and co-workers[7,8], Kabanov and co-workers[9], and certain others[10,38].

In the present review an attempt has been made to summarise the available data on the characteristic features of the polymerisation of MCM, to analyse the present state of the problem of the influence of the nature of the metal on the character of the polymerisation of such monomers, to discuss the advantages and disadvantages of the methods employed, and also to outline the most rational ways of developing this field. Attention has been concentrated on the MCM based on transition metals. As regards MCM based on non-transition metals, mention will be made of studies in which hypotheses have been developed or quantitative data are presented concerning the influence of the nature of the metal on the polymerisation or copolymerisation mechanism.

II. CLASSIFICATION AND PRINCIPAL SYNTHESES OF METAL-CONTAINING MONOMERS

In the literature there is at yet no clear-cut system of classification and nomenclature for MCM. In principle, one can employ for them the classification for traditional monomers based on the type of chain formed, the nature of multiple bonds, etc. as well as the classification based on the consideration of MCM as salts or other derivatives of the corresponding metal. However, such approaches do not reflect the specific features of the MCM and the corresponding terminology is cumbersome. From our point of view, the classification of MCM based on the type of bond between the metal and the organic component of the molecule is most convenient and yields the maximum amount of information about their structure. In terms of this principle, MCM can be divided into three main types: MCM with a covalently bonded (σ-bonded), coordinated ($n\nu$-bonded), and π-bonded metal atom, which can be illustrated by the most characteristic examples:



Here M is the metal atom, X the ligand, and Z and Y are functional groups. The first two types of MCM are characteristic of both non-transition and transition metals and the third is characteristic only of MCM incorporating Group VIA, VIIA, and VIII metals. We may note that only those π-bonded MCM in which there is a multiple bond not coordinated to the metal, in contrast to the usual fairly numerous π-complexes[11], possess the capacity for polymerisation. Metallocenes with a covalent bond between the transition metal atom and the unsaturated group have been classified as σ-bonded MCM. The type of bond has a marked influence

both on the stability of MCM and on their behaviour in polymerisation and copolymerisation processes.

The character of the polymerisation not only of organometallic monomers—compounds containing a metal–carbon bond (which is characteristic mainly of MCM of the third type)—but also a wider group of MCM incorporating metal–oxygen, metal–nitrogen, metal–phosphorus, etc. bonds is analysed in this review. The characteristic features of the polymerisation and copolymerisation of monomers incorporating both non-transition and transition metals are examined in succession for the MCM of the first and second types; as a rule, the order in which they are considered corresponds to the position of the given elements in the Periodic System.

The commonest methods of synthesis of MCM with a σ-bond involve the interaction of metal hydroxides or oxides with unsaturated acids, treatment of transition metal compounds with unsaturated alcohols, acids, and amines (see, for example, Feld and Cowe[12]), transesterification of metalloesters with an unsaturated alcohol or acid, reactions of MX_n with enolisable aldehydes or ketones, etc. Organometallic monomers are synthesised by methods involving the use of Grignard reagents containing multiple bonds in the hydrocarbon residue. We may note that methods of synthesis of MCM with a σ-bond have now been developed for almost all metals. Their stability depends both on the nature of the metal and on the structure of the MCM, procedures for the stabilisation of such compounds being known[174]. On the other hand, in contrast to MCM incorporating groups of the vinyl, allyl, and acetylene types, there are almost no literature data on MCM incorporating a metal σ-bonded to diene or allene groups.

The synthesis of MCM with a coordinate bond is based on the formation of donor–acceptor complexes of the compounds MX_n with monomers containing, apart from a multiple bond, also groups or atoms with an unshared electron pair. In terms of the nature of the coordinate bond, such MCM can be divided into compounds with nitrogen-containing ligands (vinylpyridines, vinylcarbazole, vinylimidazole, vinylbenzimidazole, vinylbenzotriazole, allyl- and diallyl-amines, acrylonitrile, etc.), oxygen-containing ligands (methyl methacrylate, methyl acrylate, vinyl acetate, methyl vinyl ketone, vinylpyrrolidone, allyl alcohol, etc.), phosphorus-containing ligands (dialkyl- and diphenyl-styrylphosphines, vinylphosphonic acids, esters, etc.), and sulphur-containing ligands (diallyl sulphide, etc.). The range of the coordination interaction energies is fairly wide and is determined by the nature of the reacting components[13]. The study of the characteristics of the formation of such MCM showed that their composition and structure do not as a rule differ from those of coordination compounds with the usual ligands. Although the donor–acceptor interaction leads to a redistribution of the electron densities of all the bonds of the monomer, a multiple bond does not usually undergo significant changes.

As regards the synthesis of MCM incorporating a π-bonded transition metal, two main methods have come to be widely used: (a) the introduction (via a series of consecutive reactions) of a vinyl, allyl, or acrylate group into the cyclopentadienyl or benzene ring; (b) the addition of MX_n to traditional monomers (for example, to styrene and its derivatives). In terms of the number of groups capable of polymerisation, the π-bonded MCM obtained can be both monosubstituted and disubstituted[4,14].

Among the non-traditional methods for the synthesis of MCM developed successfully at the present time, we may mention interesting syntheses of π-bonded MCM using the "bare" atom procedure[15]—the MCM are formed on interaction of vapours consisting of transition metal atoms at low temperatures with vinyl monomers. π-Bonded organometallic monomers, incorporating low-valence transition metal atoms, have been obtained[16] by the reductive substitution of MX_n in the presence of non-metallated monomers (for example, dienes). Metal-containing monomers of the nν- and π-types can be obtained, in principle, by a method based on the oxidative dissolution of the metals in the presence of the corresponding monomers[17]. The procedures indicated have extensive potential synthetic possibilities and their realisation will apparently make it possible to obtain a whole series of hitherto unknown MCM.

One may expect the appearance of new types of MCM, for example, those containing cyclic groups of the type of epoxy-groups, which are known at the present time for ferrocene derivatives[18] and organotin compounds[19]. The possibility of synthesising MCM with a polyfunctional type of bonding of the metal as well as polymetallic MCM appears to be promising.

Much less attention has been devoted to problems of the structure of MCM and problems of the stabilisation and destabilisation of their multiple bonds than to the synthetic aspects; however, the reactivities of multiple bonds and the methods for their activation are of outstanding interest for the polymerisation and copolymerisation of MCM.

III. HOMOPOLYMERISATION OF METAL-CONTAINING MONOMERS

MCM are polymerised (except in special cases) under the influence of a wide variety of initiators and are as a rule characterised by the same elementary steps as the polymerisation of traditional monomers. The differences are quantitative rather than qualitative. On the other hand, in an MCM–initiator system (the type of initiation can be various—radical or ionic or can involve the use of metal-complex Ziegler–Natta catalysts), the monomer can undergo reactions which are undesirable from the standpoint of the polymerisation process and can also influence significantly the active polymerisation centre.

1. Polymerisation of MCM with a σ-Bond

There are at present no publications devoted to the homopolymerisation and copolymerisation of MCM in which the vinyl group is linked directly to the metal, although such studies would be of great interest: they would be useful for the elucidation of problems concerning the influence of the metal atom on the vinyl centre, the stabilisation or destabilisation of the metal–carbon bond of the MCM in the polymer chain, etc. It may be that the difficulties are due to the elimination of a metal hydride in the polymerisation process[1]:

$$X_{n-1}M{-}CH{=}CH_2 \xrightarrow{\text{initiation}} \rightarrow\!\!- (-CH_2{-}\underset{\displaystyle MX_{n-1}}{\underset{|}{CH}}-)_t\!\!-\rightarrow X_{n-1}MH + -(-CH{=}CH-)_t\!\!- \quad .$$

On the other hand, as will be shown below, MCM with polymerisable groups of other types (allyl, acrylate, etc.) proved to be capable of polymerisation and the metal atom was retained in the resulting polymer.

(a) Homopolymerisation of MCM Incorporating a Non-transition Metal

The comparatively early studies of the homopolymerisation and copolymerisation of MCM containing alkali and alkaline earth metals, in aqueous solutions and certain other polar media, have been described in detail in a monograph[9]. The

influence of the nature of the metal atoms (even isotypical metals) on the tendency of MCM towards homopolymerisation[20-22] can be illustrated in relation to the alkali metal salts of *N*-vinylsuccinamic acid: the lithium, sodium, and potassium salts do not polymerise in aqueous and methanol solutions in the absence of initiators up to 333–353 K, the formation of a polymer being observed only in the presence of an initiator (H_2O_2). On the other hand, the rubidium and caesium salts polymerise spontaneously already in the stage involving the synthesis of the MCM, which leads to the formation of mixtures of monomeric and polymeric salts. It is striking that the tendency of these MCM towards spontaneous polymerisation increases on passing from aqueous to methanol solutions. Overall, the salts of *N*-vinylsuccinamic acid can be arranged in the following sequence in terms of the rate of formation of the polymer: Cs > Rb > Na > K > Li.

The rate of polymerisation of potassium styrene-*p*-sulphonate, the molecular weight (MW) of the polymer, and the ratios $k_p/k_t^{1/2}$ increase with increase of the ionic strength of the solution; at the same time the activation energy for polymerisation falls (from 47.9 to 30.7 kJ mol^{-1}).[23] In the concentration range 0.12–0.3 M the initial rate of the process, the molecular weight of the polymer, and the ratios $k_p/k_t^{1/2}$ in the polymerisation of the calcium, strontium, and barium salts of styrene-*p*-sulphonic acid increase in the sequence of cations $Ca^{2+} < Sr^{2+} < Ba^{2+}$.[24] With increase in the ionic strength of the solution, the rate of polymerisation rises, but the influence of the nature of the cation diminishes, which enabled the authors[24] to explain this influence from the standpoint of the electrostatic interaction between the ionised monomers and the growing polymer radicals.

The monomers do not ionise in their solid-phase polymerisation, which is usually initiated by radiation or photochemistry. Thus, on γ-irradiation (at 196 K) of potassium and rubidium acrylates, triplet lines, typical for the majority of the irradiated vinyl monomers (at least when the latter dimerise) were observed in the EPR spectra[25]. The molecular mobility of the acrylate ion in the salts is correlated with the rate of their radiation-induced postpolymerisation and increases in the sequence Na < Li ≤ K < Rb.[26] The study of the radiation-initiated polymerisation of lithium, sodium, and potassium acrylates showed[27] that potassium acrylate is polymerised fastest: even at 273 K, it polymerises faster than the lithium salt at 374 K or the sodium salt at 393 K. The rate of polymerisation of potassium acrylate decreased rapidly during the process with increase of the degree of conversion (E_a = 70.1 kJ mol^{-1}); the degree of polymerisation was almost independent of the yield of the monomer and for potassium acrylate was higher by an order of magnitude than for the sodium and lithium salts.

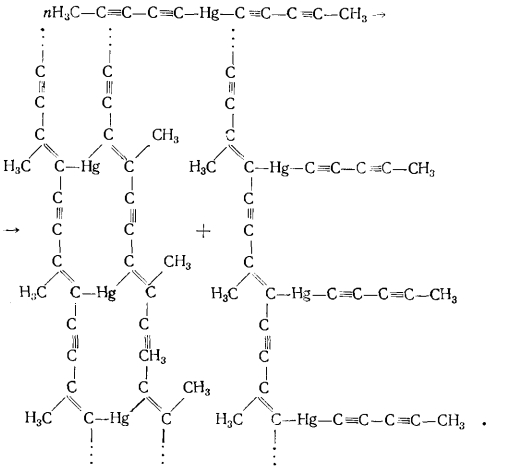
The photopolymerisation of potassium acrylate takes place effectively[28] (250–300 nm): the yield of the polymer reaches 40% at 346 K and the molecular weight diminishes from 4.7 × 10^5 to 2.2 × 10^5 with increase of the degree of conversion from 15.8 to 43.6%.

It has been noted[29] that the solid-phase radiation polymerisation of anhydrous barium methacrylate is not observed up to its decomposition temperature; the formation of only oligomeric products has been observed[30]. However, with increase of pressure, the rate of polymerisation increased (in contrast to traditional monomers such as acrylamide or methacrylamide). This has been attributed[31] to preferential polymerisation in ideal crystals. Since the rate of polymerisation is much higher when the salt hydrates are employed, it was concluded[32] that the abundance of dislocations should facilitate polymerisation. Another explanation has also been given[33]: the radicals produced by the radiolysis of the salt hydrates (water of crystallisation) contribute significantly to the formation of the free radicals initiating the solid-phase polymerisation. The yield of the polymer depends to a large extent on the degree of hydration of the salt: the maximum rate of the process is observed when calcium acrylate hemihydrate is used[32,34]. The initial rate and the limiting yield of the polymer increase in the sequence dihydrate < anhydrous salts < hemihydrate; the activation energies are 84, 38, and 4 kJ mol^{-1} respectively. The question of the influence of oxygen on this process has not so far been elucidated. According to some data[35], the rate of polymerisation is independent of the presence of oxygen (barium methacrylate dihydrate); according to other data[34], complete inhibition of the process is observed (the polymerisation of calcium acrylate dihydrate and hemihydrate as well as the anhydrous salt was investigated.) There is a possibility of postpolymerisation for calcium and barium acrylates and methacrylates[30].

In the photoinitiated (250–300 nm) polymerisation of calcium acrylate[36] the process proceeds at a constant rate up to high degrees of conversion.

The formation of coordination polymers is more characteristic of MCM containing a metal of the zinc subgroup. Studies of the polymerisation of mercury-containing monomers with a σ-bonded metal have been surveyed[38]. We shall consider only the polymerisation of one of the few MCM of the acetylenic type—bis-(1,3-pentadiynyl)mercury[37] (Scheme 1): on heating to 373–473 K, 100% conversion was rapidly attained; on ultraviolet irradiation at room temperature, the rate of polymerisation proved to be appreciably lower, because the monomer is surrounded by the polymer, which does not transmit ultraviolet light. The polymers obtained contained diacetylenic groups and exhibited different degrees of branching and cyclisation.

Scheme 1



Poly-yne polymers containing other metals (Ni, Pd, Pt) in the main chain are considered below (Section VII).

The formation of coordination polymers as well as a wide variety of condensation reactions leading to the appearance of high-molecular-weight products are more characteristic of Group III elements.

The homopolymerisation of MCM incorporating germanium, tin, and lead results as a rule in the formation of viscous oily or rubber-like products. Early studies on the polymerisation of MCM of this class have been surveyed in monographs[7,10]. Interesting results have been obtained in the investigation of the homopolymerisation of tributylstannyl methacrylate (TBSMA) in bulk (at 333 K) initiated by azobisisobutyronitrile (AIBN).[39,41]

The parameters $k_p/k_t^{1/2}$ and k_p have been estimated and compared with the corresponding parameters for methyl methacrylate (MMA): the ratios $k_p/k_t^{1/2}$ are 0.19–0.24 and 0.321, while the constants k_p (litre mol^{-1} s^{-1}) are 6.3×10^3–9.4×10^3 and 1×10^3 respectively. The fact that the rate constant for the propagation of the polymer chain is higher under comparable conditions for TBSMA than for MMA is noteworthy; this can be explained by the linear termination of the kinetic chains. Trimethylvinyltin and tributylvinyltin proved incapable of homopolymerisation[112].

The homopolymerisation of chlorodibutylstannyl acrylate is accompanied by the formation of a cross-linked polymer[42], which is probably caused by the disproportionation of the monomer, leading to dibutylstannyl dichloride and dibutylstannyl diacrylate (with polymerisation of the latter). A cross-linked polymer was also formed in the polymerisation of dimethylstannyl dimethacrylate. The polymer obtained from trimethylstannyl methacrylate was characterised by a comparatively high content of syndiotactic triads and was soluble in dimethylformamide (DMF) and methanol[43]. Triethylstannylmaleimide also polymerises via a radical mechanism[44] and, when initiating amounts of benzoyl peroxide are employed, there is no loss of the $Sn(C_2H_5)_3$ fragments from the polymer chain. At the same time a competitive interaction of the initiator with the initial monomer has been observed on increase of the concentration of benzoyl peroxide, accompanied by the cleavage of the Sn–N bond and the formation of triethyltin benzoate.

(b) Homopolymerisation of MCM Incorporating a σ-Bonded Transition Metal

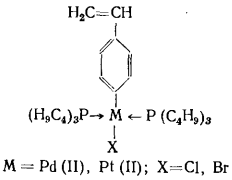
The polymerisation of polymers incorporating polyvalent transition metals is characterised by a whole series of features from the standpoint of both kinetics and the properties of the polymers formed. An even greater variety in polymerisation behaviour is characteristic of them, depending on the type and valence state of the transition metal and on the nature of the ligand groups. Thus, on being kept for several days, di-isopropoxydivinyloxytitanium polymerised spontaneously and became insoluble in heptane, while tetrastyryloxytitanium polymerises only on heating to 423 K and dihexadienyloxydi-isopropoxytitanium polymerises only on heating to 498 K.[45]

On heating in benzene in the presence of 0.1% of benzoyl peroxide, allyloxytitanocene chloride is converted into a trimer with a molecular weight of 770.[46] Polymers with a low degree of polymerisation have been isolated[47,48] on heating solutions of titanocene derivatives of methacrylic acid in DMF up to 353 K (in the presence of benzoyl peroxide as the initiator). Dimethacryloyloxy-titanocene then produced a cross-linked polymer.

It has been noted[49] that tributoxytitanium methacrylate does not polymerise in the presence of 2% of benzoyl peroxide on heating to 353–373 K. This is associated with the preferential interaction between benzoyl peroxide and alkyl orthotitanate with formation of titanium acylates[49,50]. On the other hand, in the presence of 2% AIBN, tributoxytitanium methacrylate polymerises (on heating to 423 K for 5 h), while dibutoxytitanium maleate polymerises spontaneously[51] with formation of a product having a molecular weight of 2230 (corresponding to seven monomeric units) and soluble in many organic solvents.

Among MCM with a σ-bond, containing other transition metals, copper and nickel acrylates[52] as well as zirconyl (ZrO^{2+}) methacrylate[53] proved to be capable of polymerisation. The solid-phase polymerisation of iron methacrylate takes place[54] under the influence of γ-radiation (dose rate 2.7 kJ $kg\ h^{-1}$, $T = 398$ K). Under the conditions indicated, a virtually quantitative yield of the polymer insoluble in methanol is attained after 12 h. Methacrylatopentamminecobalt(III) perchlorate polymerises with a high yield (pH 3, initiator—mixture of $K_2S_2O_8$ and $Na_2S_2O_3$).[55]

There is no information about the polymerisation of the few known σ-bonded MCM of the vanadium, chromium, and manganese subgroup metals. However, the radical polymerisation of *trans*-(4-vinylphenyl)bis(tributylphosphine)palladium chloride and bromide and the corresponding platinum compounds has been studied in comparatively high detail[56]:



M = Pd (II), Pt (II); X=Cl, Br

The polymerisation takes place under mild conditions (AIBN, 328–333 K) in benzene or toluene. White soluble polymers with molecular weights in the range 3600–10900 have been obtained, their yield depending on the polymerisation conditions. The attempts to polymerise the monomers with X = CN and C_6H_5 proved unsuccessful owing to their decomposition at the polymerisation temperature. On the other hand, their cationic polymerisation at a low temperature [in the presence of $B(C_4H_9)_3.O_2$ as the initiator] leads to the formation of polymers.

There are at present no data for the polymerisation of allene, diene, and acetylene σ-derivatives of transition metals.

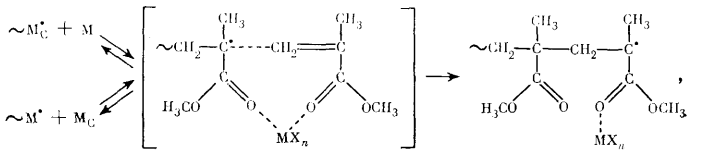
2. Polymerisation of MCM Bound in Complexes

A new branch of the field of polymerisation, based on controlling the reactions via the formation of complexes of the initial monomer with metal salts, has arisen[57,58]. In principle, the interaction between the molecules of the monomer and the complex-forming agent can influence radically all the stages of the polymerisation process. The monomer then becomes "chemically activated" fairly frequently. The chemical activation can be associated both the intramolecular and intermolecular effects. As a consequence of this, there is as a rule an appreciable increase of the rate of polymerisation. In the problem considered, it is possible to distinguish three main components, each of which has its own specific features:
(a) polymerisation of vinyl monomers bound in complexes;
(b) polymerisation of allyl monomers bound in complexes;
(c) polymerisation of heterocycles bound in complexes.

(a) Characteristic Features of the Polymerisation of Vinyl Monomers Bound in Complexes

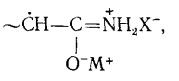
The influence of MX_n on polymerisation depends on the nature of the metal and the monomer, the method used to initiate polymerisation, and the ratio $[MX_n]/[\text{monomer}]$ in the system. $ZnCl_2$ is most frequently used as the complex-forming agent in the polymerisation of such MCM. Thus, is the polymerisation of MMA in the presence of $ZnCl_2$ or $AlCl_3$ (with initiation by AIBN at 323 K or by the photochemical decomposition of azo-compounds) in the presence of low contents of MX_n, the rate of the process increases linearly with the increase of the ratio $[MX_n]/[MMA]$ up to 0.2, after which there is some non-linear increase of the rate of polymerisation[59]. With increase of the ratio $[MX_n]/[MMA]$ under these conditions, k_p also increases, while k_t hardly changes; for $[MX_n]/[MMA] > 0.25$, k_p begins to diminish, while k_t falls sharply (by two orders of magnitude). An appreciable increase of the rate

of polymerisation of other vinyl monomers (4-vinylpyridine, 2-vinylpyridine, methylvinylpyridine, and acrylonitrile) has also been noted in the presence of $ZnCl_2$.[60] The complex-forming agent is regarded[59] as a "complementary species" involved in the formation of the transition complex (a coordination-radical mechanism of the propagation reaction obtains):



where M_c and M_c^* are the monomer and the growing radical bound in the complex respectively. One cannot exclude from consideration the possibility of the formation of organised aggregates of monomers bound in complexes (labile seeds) containing units with a suitable steric arrangement for polymerisation (an intermolecular effect)[61].

The importance of steric organisation is also confirmed by data for the solid-phase polymerisation of acrylamide and its *N*-alkyl derivatives bound in complexes with zinc halides. The polymerisation of the complexes is accompanied by an appreciable (by a factor of 1.5–2) increase of E_a.[104] This is attributed to the fact that the distance between the monomer molecules in the crystals of the pure monomer is much smaller than in the crystal of the complex. It is of interest that the polymeric complexes obtained have a linear structure, in contrast to the highly cross-linked polymers formed in the polymerisation of acrylamide derivatives not bound in complexes. The significant (by a factor of 3–5) increase of the rate of homopolymerisation of these monomers in the presence of lithium, calcium, and zinc salts is attributed to changes in the ratio $k_p/k_t^{1/2}$.[197] The increased activity of the radical incorporated in the complex has been explained[198] by the formation of the structure



characterised by an increase localisation of the unpaired electron at a carbon atom.

The homopolymerisation of vinyl monomers [particularly various vinylpyridines (VP)] bound in complexes with transition metal salts has been investigated in fair detail. Thus the complexes of cobalt and nickel chlorides were found to undergo solid-phase polymerisation[62]: $Co(4\text{-VP})_2Cl_2$ polymerised on heating to 380–405 K and in the presence of AIBN the reaction was appreciably accelerated; $Co(4\text{-VP})_4Cl_2$ and $Co(2\text{-VP})_2Cl_2$ polymerise on photochemical initiation. The polymerisation of adducts of $CoCl_2$ with various vinylpyridines (DMF, AIBN, 323 K) has also been studied[263]. Their polymerisation behaviour proved to be qualitatively similar to that of the $ZnCl_2$ complexes[64]. On the other hand, the nickel complexes show less tendency towards polymerisation: $Ni(4\text{-VP})_4Cl_2$ decomposes to $Ni(4\text{-VP})_2Cl_2$, which polymerises at 353–403 K on the surface of the crystals, forming a small amount of the polymer[62]. On heating to 353 K, the complexes $Cu(2\text{-VP})_2Cl_2$ and $Cu(2\text{-VP})Cl_2$ decompose with dissolution in their own ligand without any polymerisation, while $Cu(4\text{-VP})_2.Cl_2$ undergoes thermal polymerisation.

The interaction of tungsten, cobalt, and manganese carbonyls with 4-VP leads to the thermal polymerisation of the latter[65]. The possibility of the polymerisation of 4-VP bound in a complex with ruthenium(II) [of the complexes *cis*-$Ru(bipy)_2.(4\text{-VP})X^{n+}$, where $n = 1$ and X = Cl or $n = 2$ and X = CO or 4-VP] has been demonstrated[66]; the properties of the resulting polymers were not described in the above communication.

When vinylpyridines are polymerised in the presence of MX_n, the polymerisation of 4-VP and methylvinylpyridine is accelerated, while that of 2-VP is sharply retarded[63,64]. The accelerating effect in the first two instances has been attributed to the increase of k_p owing to the heterogenisation of the polymeric system, while steric effects, resulting in the shielding of the vinyl group, play a significant role for 2-VP.

For other MCM, we may note the radical polymerisation of bis(1-vinylimidazole)-manganese dichloride in aqueous methanol[67]. It is striking that $MnCl_2$ is a more effective complex-forming agent than HCl and CH_3I: when HCl in the complex was replaced by $MnCl_2$, the rate of polymerisation increased by a factor of 4.5†. It has been suggested[69] that, as a consequence of the intense dynamic conjugation of the π-electron systems of the vinyl group and the heterocycle, the coordination of vinylimidazole with $MnCl_2$ results in an increase of the polarity of the double bond and of the polarity factor *e*. An increase of the ratio $k_p/k_t^{1/2}$ has also been noted in the polymerisation of coordinated vinylimidazole, which may be due to the decrease of k_t owing to the increase of the molecular mobility of the polymer chains bound in a complex.

The synthesis of the polymeric complexes can be greatly facilitated as a result of the free-radical polymerisation of 1-vinylazoles in the presence of the corresponding metal chloride added to the reaction mixture[68,70]. In this case the complex formation and polymerisation reactions take place simultaneously. The composition of the polymer unit usually corresponded under these conditions to the ratio of the initial components. Thus in an alcoholic solution it was possible to obtain polymers from the following systems: vinylimidazole–$MnCl_2$, vinylimidazole–$NiCl_2$, vinylbenzimidazole–$NiCl_2$; vinylbenzotriazole–$NiCl_2$. Comparison of the effects of the nature of the ligands showed that polymerisation takes place more efficiently when vinylimidazole is used as a monomer.

In an aqueous medium in the presence of copper, iron, nickel, cobalt, and manganese salts the polymerisation of MMA is accelerated[72]. It has been noted that the cation is of decisive importance in this effect, its activity varying in the sequence $Cu^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+} > Co^{2+}$, while the influence of the anion proved to be weaker. The results have been explained by the formation of the corresponding complexes. The homopolymerisation of complexes of palladium and nickel halides with vinylpyridine and phosphorus-containing monomers has been described[73].

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†On the other hand, it had been shown in an earlier study[68] that the complexes $M(vinylimidazole)_4Cl_2$ (M = Mn, Co, or Ni) show a smaller activity in free-radical polymerisation than the non-coordinated vinylimidazole; for example, under identical conditions (4% AIBN, 343 K, alcohol), the degree of conversion of vinylimidazole reached 75%, while those of its complexes with the manganese and nickel chlorides reached only 60 and 35% respectively. Furthermore, analogous complexes with iron and copper chlorides could not be converted into polymeric products at all; evidently in this case the radicals formed are inhibited. The yields of the polymeric complexes obtained from $Ni(vinylbenzimidazole)_2Cl_2$ and $Ni(vinylbenzotriazole)_2Cl_2$ were low.

(b) Polymerisation of Allyl Monomers Bound in a Complex

The approach based on the polymerisation of compounds bound in complexes has been used particularly successfully in the case of allyl monomers. The polymerisation of allyl monomers is known[74] to involve considerable difficulties associated with the effective degradive chain-transfer, which results in the formation of the relatively inactive allyl radicals:

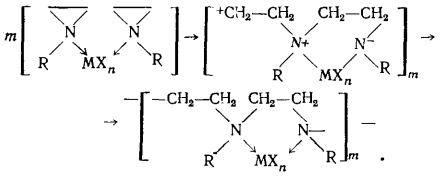
$$R^{\cdot} + H_2C{=}CH{-}CH_2X \rightarrow RH + H_2C{=}CH{-}C^{\cdot}HX \ .$$

On the other hand, the radical-initiated polymerisation of allyl monomers bound in complexes with metal salts proceeds at higher rates and with formation of polymers having high molecular weights. It has been suggested[75] that complex formation promotes the establishment of the steric conditions necessary for the reaction of the monomer and the radical, which are both ligands within the same coordination complex (intramolecular effect). Under these conditions, there is a possibility, firstly, of a decreased probability of the abstraction of a hydrogen atom by the growing radical and, secondly, the coordinated chain-transferring allyl radical formed in this instance may be capable of cleaving the double bond of the monomer (for example, as a consequence of the decrease of the rate of destruction of such species).

Various non-transition metal salts are used as complex-forming agents for allyl monomers[75-77]: LiCl, $LiNO_3$, Na_2SO_4, $MgCl_2$, $ZnCl_2$, and $ZnBr_2$. Among the few studies in which transition metal salts have been used as complex forming agents, we may mention one[78] on the radical polymerisation of allyl alcohol in the presence of chromium salts[78]. The rate of the process was found to decrease by a factor of 14.8 [$CrCl_3$, 348 K, $(NH_4)_2S_2O_8$]. The observed decrease of the reaction orders with respect to the initiator and the monomer (from 1.8 to 0.8 and from 0.5 to 0.4 respectively) has been attributed[78] to the involvement of the complex-forming agent in the elementary stages of the process and to the consequent increase of the probability of the transition from the degradative chain transfer to effective chain transfer.

(c) Polymerisation of Heterocycles Bound in a Complex

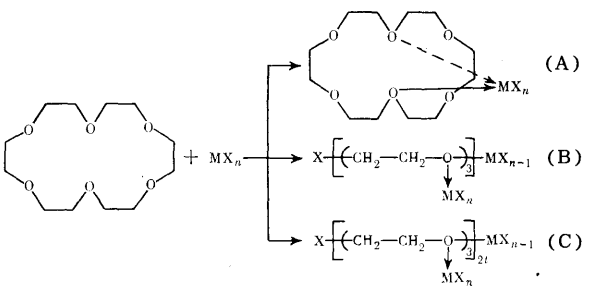
The redistribution of electron densities at the atoms and bonds in heterocycles as a consequence of complex formation, makes possible the occurrence of specific chemical reactions of the heterocycles in the coordination sphere of MX_n, which results in the formation of polymeric complex macromolecules. This can be demonstrated in relation to the $ZnCl_2$, $CdCl_2$, $PdCl_2$, $CoCl_2$, etc. complexes with ethyleneimine and and its derivatives[79-81]. Complex formation, the strain in the ethyleneimine ring increases by approximately 42 kJ mol^{-1}, which leads to a sharp decrease of the strength of the endocyclic bonds. Such complexes are capable of thermal polymerisation (both in bulk and in aprotic solvents) with opening of the heterocycle via a mechanism involving the heterolytic cleavage of the C–N bonds with formation of dipolar coordination ions:



The coordinate bonds are retained in the polymerisation process, which leads to the formation of polymeric chelate complexes. The characteristic features of such reactions are the presence in the initial complexes of at least two# heterocycles in the coordination sphere of the metal on the one hand, and the existence of "critical" temperatures for the dissociation of bonds in the heterocycles on the other.

The interaction of MX_n with macrocyclic crown-ethers takes place in an even more complex manner[82,83], involving the formation of three types of products (Scheme 2): (A)—the complexes of the $n\nu$ type produced by the exocyclic coordination of an MX_n molecule with two oxygen atoms; (B)—products of the opening of the crown-ether ring; (C)—polymers which are probably formed via a cationic polymerisation mechanism (the degree of polymerisation reaches 3–4).

Scheme 2



The amounts of fractions (A), (B), and (C) in the products of the reaction of dibenzo-18-crown-6 with $TiCl_4$, VCl_4, and $MoCl_5$ are respectively (wt.%) 87.5, 4.5, and 8.0 for (A), 60.0, 20.0, and 20.0 for (B), and 64.0, 24.0, and 12.0 for (C). It may be that similar reactions take place also for other types of heterocycles bound in complexes.

Thus the polymerisation of MCM bound in complexes is one of the most thoroughly investigated branches of the chemistry of MCM and not only theoretical but also practical possibilities of this field have already been outlined: the regulation of the molecular weights of the polymers obtained (which is particularly important for monomers of the allyl type), the acceleration of the process, the increased degree of conversion of the monomers, and the opening and polymerisation of heterocycles. There is every reason to believe that this field will develop vigorously in the future.

3. Homopolymerisation of π-Bonded MCM

In this class of MCM, the homopolymerisation (using different initiation methods) of vinylferrocene has been most fully investigated[1,4,5]. The principal conclusions reached in the study of the polymerisation of this monomer reduce to the following. With radical initiation in the presence of AIBN there is intramolecular electron transfer from the iron atom to the radical centre with formation of an Fe(III)-containing terminal group, which is accompanied by intermolecular chain termination. The order of the polymerisation reaction with respect to the initiator is therefore unity and the molecular

#The reactions of complexes containing one heterocycle in the coordination sphere terminate with the formation of cyclic dimers (piperazine derivatives); complexes incorporating a heterocycle and a primary or a secondary amine are incapable of polymerisation.

weight of the polymer does not increase with decrease of the initiator concentration. This has been explained[4] by the high chain transfer constant ($k_{tr}/k_p = 8 \times 10^{-3}$ compared with 6×10^{-5} for the polymerisation of styrene at 333 K); the high value of k_{tr} leads to the branching of the polymer formed.

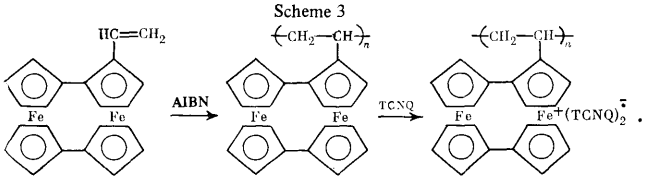
Vinylferrocene provides an example of the influence of the transition metal in the MCM molecule on the character of its polymerisation. Thus the introduction of separating bridges between the ferrocenyl and active vinyl groups (as, for example, in ferroceynyl methacrylate) leads to the usual chain termination mechanism for which the dependence of the rate on the initiator concentration corresponds to a reaction order of 0.5.

The radical polymerisation of vinylcyclopentadienyltricarbonylmanganese[84] (benzene, AIBN) results in the formation of a polymer with MW > 2500. Its thermal polymerisation in bulk (at 443 K) leads to the formation of a glassy polymer. The unusual kinetic features of the polymerisation of this monomer in benzonitrile have been noted: the rate of polymerisation is given by the equation $w_{pol} = k_p[M]^2[AIBN]$ but an explanation for this has not yet been found.

η^5-Vinylcyclopentadienyldicarbonylmolybdenum and the corresponding tungsten compound are capable of homopolymerisation[85]. It is of interest that η^5-vinylcyclopentadienyldicarbonylcobalt does not polymerise owing to the decomposition of the organometallic component of the molecule, while the analogous iridium monomer gives rise to a homopolymer containing up to 50 wt.% of the metal.

The reasons why styryltricarbonylchromium does not polymerise either via a radical mechanism or in the presence of LiC_4H_9 have not as yet been elucidated; at any rate they are not steric. The transition state is probably stabilised in this instance by the strong (contact or resonance) interaction of the active centre with the $Cr(CO)_3$ group. On the other hand, η^6-(benzyl acrylate)-tricarbonylchromium readily polymerises in tetrahydrofuran (THF) (AIBN, 328–343 K), forming polymers with different molecular weights[86]. The homopolymer obtained in ethyl acetate had a molecular weight of 1.5×10^4. Among the η^4-dienylmetal tricarbonyl MCM, only η^4-(hexa-2,4-dien-1-yl acrylate)tricarbonyliron polymerises effectively (AIBN, benzene).[87] The considerable role of the reaction involving chain transfer to the polymer (particularly at high monomer concentrations), which leads to the formation of a polymer with a branched structure and a broad molecular weight distribution and partly to the formation of a microgel, has been noted. Among other MCM incorporating π-bonded iron, we shall mention the radical polymerisation of 3-vinylfulvalene(fulvalene)di-iron (Scheme 3) (solution in benzene, 343 K 24 h, yield 18%).[88] A characteristic feature of the polymer formed, which has a molecular weight of 5000 (average degree of polymerisation 18), is that, following its oxidation by tetracyanoquinodimethane (TCNQ), it acquires an exceptionally high conductivity for organic polymers, amounting to $(6–9) \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$:

Scheme 3



More than 70% of the iron in the polymer is oxidised; the product consists of the mixed-valence salt $[Fe^{II}Fe^{III}][TCNQ]_2$. According to the results of physicochemical studies[88], the bisfulvalenedi-iron unit incorporating TCNQ constitute a delocalised system with only one type of iron atoms having a formal degree of oxidation of 2.5.

The homopolymerisation of η^5-(vinylcyclopentadienyl)-methyltricarbonyltungsten (AIBN, benzene, 333 K) has been investigated[89–91]. The operation of two different mechanisms of the polymerisation of this monomer was proposed initially: the traditional mechanism involving the vinyl bond and an unusual mechanism consisting in the initiation of the process by the $WCH_2^{\cdot}$ radical, formed via the intramolecular elimination of a hydrogen atom from the WCH_3 group. However, in a later study[85] the authors concluded that the traditional mechanism of vinyl polymerisation in fact operates. The process proceeds with difficulty up to molecular weights of 14000 with a high degree of consumption of the initiator, which corresponds to the kinetic process equation $w_{pol} = 1.13 \times 10^{-2}\ [AIBN]^{2.3}[M]^{0.8}$.[91] Such a high reaction order with respect to the initiator was not explained theoretically[91]. The calculated activation energy for chain propagation proved to be extremely high (338 kJ mol^{-1}).

A final conclusion concerning the influence of the metal atom on the elementary stages of the polymerisation of MCM apparently requires additional studies. The data available at the present time make it possible to conclude only that such influence is highly individual and depends on the type of bonding of the metal to the MCM, the nature of the metal itself, its ligand environment, and its valence state. As a rule, the MCM are highly active in chain transfer and termination reactions, although the mechanism of their action is still not clear. One can only conclude confidently that spatial separation of the multiple bond and the metal atom diminishes this effect. There are no direct data concerning the mutual influence of the metal atoms incorporated in the polymer chain.

There is virtually no information about the stereospecific polymerisation of MCM, although on general grounds it is not difficult to postulate that the metal atom is able to influence the orientation of the MCM molecule in the course of its addition to the growing chain and hence can influence the formation of stereoregular polymers.

IV. COPOLYMERISATION OF METAL-CONTAINING MONOMERS

A whole series of MCM incapable of homopolymerisation or polymerising with difficulty to oligomers are capable of copolymerising effectively with other monomers. One should note that there have been virtually no systematic studies of the radical polymerisation of MCM which would permit the calculation of the corresponding copolymerisation constants (r_1 and r_2) and the determination of the influence of the transition metal on their values and there have been no calculations of the parameters Q (a measure of the resonance stabilisation of the monomer during copolymerisation) and e (a measure of the polarity of the substituent at the double bond) in the Alfrey–Price mechanism. The only exceptions are the metallocene MCM [1,4] and the styryl-substituted palladium compound mentioned above[56].

1. Copolymerisation of σ-Bonded MCM Incorporating a Non-Transition Metal With Traditional Monomers

The rate of copolymerisation of MMA with alkali metal methacrylates (methanol, 333 K, AIBN) decreases with increase of the size of the cation[92]. It is striking that there is a clear-cut tendency towards the alternation of monomers in the MMA–lithium methacrylate copolymer: $r_1r_2 = 0.044$. An

alternating copolymer has also been obtained in the copolymerisation of acrylamide with sodium acrylate[93]. The composition of the copolymer obtained by the copolymerisation of the sodium salt of allenesulphonic acid with acrylonitrile in DMF was not described adequately[94]: apparently the parameters of the activity of the monomers varied with the initial molar ratio of the monomers.

The structure of such metal-containing polymers has been investigated. Thus it has been shown by Raman spectroscopy (absorption band in the range 166–170 cm^{-1}) [95,96] that, in the styrene–sodium methacrylate copolymer, the cations and anions are aggregated into clusters, particularly in the presence of a high metal content. Unfortunately the mechanism of their formation and the nature of the bonds in such aggregates have not so far been adequately studied.

The copolymerisation of alkaline earth metal acrylates with traditional vinyl monomers has been investigated in fair detail. Thus calcium, strontium, and barium acrylates have been copolymerised in aqueous solution with acrylamide and methacrylamide (mixture of $K_2S_2O_8$ and $Na_2S_2O_5$, 303 K).[97,98] The quantity r_2 varied in the sequence $Ba^{2+} < Ca^{2+} < Cr^{2+}$, while r_1 varied in the sequence $Ba^{2+} > Ca^{2+} \cong Sr^{2+}$. The overall rate of copolymerisation decreases with increase of the MCM concentration. Other conditions being equal, the rate of the process fell to a greater extent after the addition of barium acrylate than after the introduction of calcium and strontium acrylates. These facts have been attributed[97,98] to the electrostatic interaction between the growing macroradicals and the acrylate ions, which depends significantly on the interaction of the Ca^{2+}, Sr^{2+}, and Ba^{2+} cations with segments of the polyacrylamide chain in the macroradical (as for alkali metal acrylates). Similar results have been obtained also in the study of the emulsion copolymerisation of styrene with strontium acrylate initiated by $K_2S_2O_8$:[99] with increase of the MCM concentration to values exceeding 0.5%, the yield of the copolymer diminishes sharply. A reaction mechanism has been proposed in which account is taken of the growth of the macroradicals in different phases and the formation of the copolymer mainly as a result of the recombination of these macroradicals at the water–micelle interface is postulated.

The few studies of the catalytic copolymerisation of MCM merit special attention. For example, the copolymerisation of calcium acrylate with ethylene under the influence of the Ziegler–Natta catalytic systems $(RO)_2TiCl_2$–$Al(C_2H_5)_{1.5}Cl_{1.5}$, where R = n-C_4H_9, iso-C_4H_9, or iso-C_3H_7, has been investigated. For R = n-C_4H_9 or iso-C_4H_9, the yield of the copolymer did not change following an increase of the MCM concentration from 0.04 to 0.012 M, while for R = iso-C_3H_7 the yield fell appreciably. The reactivity of the calcium salt proved to be lower by a factor of two than that of the potassium salt. The calcium content in the copolymer depended on the structure of the alkoxy-group in $(RO)_2TiCl_2$ and increased in the sequence iso-C_3H_7O < iso-C_4H_9O < n-C_4H_9O. The observation of the influence of steric factors and allowance for this influence make it possible to diminish the effect of the polar monomer on the catalytic system in copolymerisation (this problem will be examined in greater detail below§).

The opposite examples, in which the rate of copolymerisation increased with increase of the MCM content in the reaction medium, are also known—for example[103] in systems comprising MMA, styrene, or 2-hydroxyethyl methacrylate, on the one hand, and the zinc or cadmium salt of ethylene methacrylate phthalate, on the other:

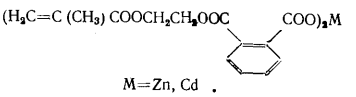


Table 1. The relative reactivity constants of tin-containing monomers M_1 in copolymerisation with traditional monomers M_2.

M_1	M_2	Conditions	r_1	r_2	$r_1 \cdot r_2$	Refs.
$(CH_3)_3Sn(CH=CH_2)$	St	AIBN, benzene, 323 K	0.001	44.8	0.0448	[112]
$(CH_3)_3Sn(CH=CH_2)$	MMA	ditto	0.03	25.1	0.753	[112]
$(C_4H_9)_3Sn(CH=CH_2)$	St	»	0 005	16.0	0.08	[112]
$(C_4H_9)_3Sn(CH=CH_2)$	MMA	»	0.03	27.9	0.837	[112]
$(CH_3)_3Sn(OOC(CH_3)=CH_2)$	St	AIBN, DMF, 333 K	0.53	1.57	0.832	[43]
$(CH_3)_3Sn(OOC(CH_3)=CH_2)$	MAN	ditto	0.20	0.0	0.0	[43]
$(CH_3)_3Sn(OOC(CH_3)=CH_2)$	MAN	BP, 333 K, in oil	0.220	0	0	[114]
$(C_2H_5)_3Sn(OOC(CH_3)=CH_2)$	MAN	ditto	0.122	0	0	[114]
$(C_3H_7)_3Sn(OOC(CH_3)=CH_2)$	MAN	»	0.081	0	0	[114]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	MAN	»	0.053	0	0	[114]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	MA	AIBN, toluene, 343 K	1.738	0.657	1.142	[111]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	EA	ditto	1.261	0.610	0.768	[111]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	BA	»	0.851	0.575	0.489	[111]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	AN	»	0.468	0.471	0.220	[111]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	MMA	»	0.79	1.0	0.79	[110]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	PMA	»	0.58	0.9	0.52	[110]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	BMA	»	0.65	0 68	0.442	[110]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	VPr	»	3.160	0.438	1.384	[107]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	VA	»	4.408	0.017	0.0749	[107]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	St	»	0.258	1.106	0.2848	[108]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	AMA	»	2.343	1.035	2.4258	[108]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	GA	»	1.356	0.367	0 4977	[109]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	GMA	»	0.754	0.794	0 5987	[109]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	MAA	»	4.230	0.381	1.6116	[109]
$(C_2H_5)_3Sn(OOCC(CH_3)=CH_2)$	MMA	AIBN, benzene, 333 K	0.705	0.37	0.261	[113]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	MMA	333 K	0 93	1.04	0.9672	[40]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	VA	333 K	0.76	0.028	0.0213	[40]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	St	333 K	0.40	1.14	0.4560	[40]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	MA	AIBN, DMF, 323 K	0.03	0.82	0.0246	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	EA	ditto	0.08	0.75	0.0600	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	BA	»	0.15	0.70	0.1050	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	OA	»	0.23	0.66	0.1141	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	MA	aqueous emulsion, 345 K	0.51	1.97	1.0047	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	EA	ditto	0.41	0.89	0.3650	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	BA	»	0.42	0.73	0.3086	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	OA	»	0.49	0.67	0.3283	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	MMA	AIBN, toluene, 343 K	0.398	2.190	0.8714	[106]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	PMA	ditto	0.319	1.699	0.5410	[106]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	BM	»	0.196	1.659	0.3260	[106]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	AN	»	0.242	1.003	0.2421	[106]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	VPr	»	2.567	0.006	0.0154	[107]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	VA	»	0.517	0.610	0.3129	[107]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	St	»	0.213	1.910	0.4157	[108]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	AMA	»	0.195	2.257	0.4883	[108]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	GA	»	0.295	1.409	0.4157	[109]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	GMA	»	0.344	4.290	1.4758	[109]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	MAA	»	0.977	1.258	0.2291	[109]
$(C_4H_9)_2(Cl)Sn(OOCCH=CH_2)$	MA	AIBN, benzene, 333 K	0.08	0.81	0.065	[42]
$(C_4H_9)_2(Cl)Sn(OOCCH=CH)$ | C_6H_5	MA	ditto	0	2.0	0	[42]
$(CH_3)_2Sn(OOCC(CH_3)=CH_2)_2$	St	AIBN, DMF, 333 K	0.83	0.28	0.232	[40]

Notation: MAN = maleic anhydride, MA = methyl acrylate, EA = ethyl acrylate, BA = butyl acrylate, OA = octyl acrylate, AN = acrylonitrile, PMA = propyl methacrylate, BMA = butyl methacrylate, AMA = allyl methacrylate, GMA = glycidyl methacrylate, GA = glycidyl acrylate, N-MAA = *N*-hydroxymethylacrylamide, St = styrene, VPr = vinylpyrrolidinone, and VA = vinyl acetate.

§ We may note that catalytic systems based on alkoxy-derivatives of titanium combined with organoaluminium components generate free radicals under the influence of polar monomers (for example, MMA)[102]; the radicals can alter the polymerisation process.

In systems containing MMA, copolymerisation proceeds faster than in systems containing styrene: complete conversion is attained after several hours, but after 15–30% conversion gelling of the system takes place.

Table 2. The values of Q and e in the Alfrey–Price mechanism for the copolymerisation of Sn-monomers.

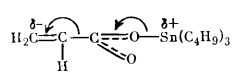
M_1	M_2	Q	e	Refs.
$(CH_3)_3Sn(CH=CH_2)$	St	0.005	0.962	[112]
$(CH_3)_3Sn(CH=CH_2)$	MMA	0.036	0.933	[112]
$(C_4H_9)_3Sn(CH=CH_2)$	St	0.017	0.822	[112]
$(C_4H_9)_3Sn(CH=CH_2)$	MMA	0.031	0.822	[112]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	alkyl acrylates	0.23	−0.5	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	alkyl acrylates*	0.23	−0.1	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	**	0.235	0.401	[109]
$(CH_3)_3Sn(OOCC(CH_3)=CH_2)$	St	0.45	−0.37	[43]
$(CH_3)_3Sn(OOCC(CH_3)=CH_2)$	MAN	0.31	−0.64	[114]
$(C_2H_5)_3Sn(OOCC(CH_3)=CH_2)$	MAN	0.27	−0.75	[114]
$(C_4H_7)_3Sn(OOCC(CH_3)=CH_2)$	MAN	0.23	−0.81	[114]
$(C_4H_9)_3Sn(OOCC(CH_3)=CH_2)$	MAN	0.18	−0.88	[114]
$(C_4H_9)_3Sn(OOCC(CH_3)=CH_2)$	**	0.852	0.197	[109]
$(CH_3)_2Sn(OOCC(CH_3)=CH_2)_2$	St	1.36	0.41	[43]

*Emulsion copolymerisation.
**Values obtained by averaging the data for glycidyl acrylate, glycidyl methacrylate, and *N*-hydroxymethylacrylamide.

The copolymerisation of tin-containing MCM, mainly trialkylstannyl acrylates, has been investigated in greatest detail, the copolymerisation constants for such monomers being summarised in Tables 1 and 2. The following features of the copolymerisation of tributylstannyl acrylate (TBSA) with alkyl acrylates have been discovered[105].

1. The rate of the process decreases with increase of the length of the alkyl chain of the alkyl acrylate and with the fraction of TBSA in the monomer mixture.

2. The alternation of units, confirmed by the S-shaped curves for the composition of the monomers and the values of r_1 and r_2 less than unity, is observed; such alternation is due to the negative polarisation of the double bond in the TBSA molecules and the positive polarisation in alkyl acrylates. The negative polarisation of the double bond in TBSA is due to the concentration of a considerable negative charge at the oxygen or tin atom, which is transferred inductively to the double bond, indicating a high polarity of the =–Sn bond:



3. The fraction of TBSA in azeotropic monomer mixtures increases with increase of the length of the alkyl chain of the alkyl acrylate owing to the decrease of activity in the series of alkyl acrylates.

It is of interest that TBSA and chlorodibutylstannyl acrylate have similar values of r_1 and r_2 in copolymerisation with methyl acrylate[42 105], which indicates the same influence of the C_4H_9 and Cl groups at the tin atom on the reactivity of the multiple bond.

The rate of copolymerisation of trialkylstannyl acrylates with maleic anhydride passes through a maximum for the equimolar composition of the monomer mixtures[19,71,114]. The constant $r_2 = 0$ for all the sytems, r_1 and Q decrease, and e_1 increases with increase of the length of the alkyl group in MCM. It has been suggested that the formation of the alternating copolymers is due to the interaction of the tin atom of the metal-containing monomer with the carbonyl group of maleic anhydride in the transition complex arising in the chain propagation reaction[19]. Under these conditions, the tendency of trialkylstannyl methacrylates to form complexes increases with increased length of the alkyl substituents at the tin atom, while the rate of their copolymerisation with maleic anhydride diminishes. It has been shown[44] that the copolymerisation of *N*-trialkylstannylmaleimide with styrene results in the formation of copolymers with a strict alternation of the monomeric units over a wide range of conversions and molar ratios of the monomers.

The following tin-containing terpolymers have also been synthesised: TBSA–vinyl acetate–vinylpyrrolidinone, TBSMA–vinyl acetate–vinylpyrrolidinone[107], TBSA–methyl methacrylate–acrylonitrile, TBSA–butyl methacrylate–acrylonitrile[111], TBSA–styrene–acrylonitrile, and TBSM–butyl methacrylate–acrylonitrile[108], the composition of the copolymers corresponding to the copolymerisation constants.

2. Copolymerisation of σ-Bonded MCM Based on Transition Metals

Tetramethylallyloxytitanium does not polymerise (either in the absence or presence of additives such as $SnCl_4$ and BF_4), but its copolymer with vinyl acetate has been obtained[115] (at room temperature without adding initiators), although the latter is incapable of homopolymerisation at room temperature. The same effect has been observed for the copolymerisation of trichlorotitanium acrylate with styrene (the reaction takes place explosively even in a dilute solution) or with isoprene[116]. The monomer itself is apparently a catalyst of cationic polymerisation in such cases. The copolymer of tetramethylallyloxytitanium with MMA has been obtained[115] in the presence of benzoyl peroxide at 338 K. The yellow solid polymer formed proved to be insoluble in solvents specific for poly(methyl methacrylate).

Tributoxytitanium methacrylate copolymerises (benzoyl peroxide, 363 K) with MA, while dibutoxytitanium dimethacrylate and dibutoxytitanium maleate copolymerise with styrene under the same conditions[51]. The possibility of the radical copolymerisation of a butenoxy-derivative of titanium with vinyl monomers has been noted[12]. The copolymerisation of allyloxytitanocene chloride[46] with styrene or MMA (monomer molar ratio 1:10, 0.5% of benzoyl peroxide, 373–393 K) leads to the formation of solid transparent orange copolymers with molecular weights of 22100 and 70000 respectively [the molecular weights of the polystyrene and poly(methyl methacrylate) obtained under the same conditions were 50000 and 90000 respectively]. These data confirm the conclusion that the MCM are highly active also in reactions involving the transfer of the growing chains. Infrared spectroscopic data indicate the retention of the titanocene structure in the copolymer[46]. The copolymerisation of methacryloyloxytitanocene chloride and also dimethacryloyloxytitanocene with the same monomers confirms these conclusions[48].

The copolymerisation of zirconyl methacrylate and acrylate[53] with styrene and various alkyl acrylates to form cross-linked copolymers insoluble in organic solvents and having a softening temperature higher than for the corresponding homopolymers, namely polystyrene and poly(alkyl acrylate), has also been reported[53]; however, quantitative data have not been published.

It has been noted[117] that the gelling of the ethylene glycol–chromium(III) methacrylate phthalate–styrene system (peroxide type initator, 328–373 K) beings already after 10–20%

conversion. Copolymers insoluble in the usual solvents were formed also in the radical copolymerisation of butoxy(methyl methacrylate)(ethylene glycol)titanium with styrene[118].

Data are available for the radical (comonomer–vinylpyrrolidinone, AIBN, solution in DMF, 323–353 K) and cationic (comonomer–α-methylstyrene, BF_3) copolymerisation of metalloporphyrin[119] and chlorophyll-containing[120] MCM.

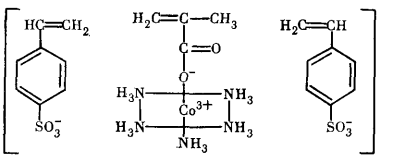
The copolymerisation of *trans*-(4-vinylphenyl)bis(tributylphosphine)palladium chloride (benzene, AIBN, 328 K) has been investigated in detail[56]. The parameters $r_1 = 1.49$ (styrene) and $r_2 = 0.45$ were calculated by the Fineman–Ross equation for low degrees of conversion, which led to $Q = 0.41$ and $e = -1.4$ for the Alfrey–Price mechanism (the corresponding values for styrene are 1.0 and −0.8). The value of e_1 shows that, on the basis of the equation for the correlation between e and the Hammett constant, the σ-bonded palladium gro:p in *p*-substituted styrene is highly electron donating, of the type of *p*-amino- or *p*-methoxy-group in an aromatic ring. It might have been expected that *trans*-(4-vinylphenyl)bis(tributylphosphine)palladium dichloride would manifest a high reactivity in cationic polymerisation owing to the negative value of e, but BF_3 etherate did not induce its polymerisation, which was explained[56] by the interaction of the palladium group with BF_3, leading to the inhibition of the homopolymerisation.

Table 3. The copolymerisation constants and the parameters Q and e for the copolymerisation of methacrylatopentaamminecobalt(III) perchlorate (I) and *cis*-dimethacrylatotetra-amminocobalt(III) perchlorate (II) with methacrylic acid (aqueous solution, 303 K, $K_2S_2O_8 + Na_2S_2O_3$ initiator). [55]

Monomer	pH	r_1	r_2	Q	e
(I)	3	0.02±0.02	3.8±0.4	0.17	−0.91
(II)	3	0.001±0.001	2.1±0.5	0.17	−1.8
(I)	7	0.8±0.3	0.15±0.1	1.4	+0.46

Interesting features were observed[55] in a study of the radical copolymerisation of methacrylatopentamminecobalt(III) perchlorate and *cis*-dimethylacrylatotetramminecobalt(III) perchlorate with methacrylic acid. Table 3 shows that the pH of the medium has a significant influence on the copolymerisation process. This is probably associated with the fact that 90% of methacrylic acid is ionised at pH 7 and only 3% is ionised at pH 3. Accordingly, in the former case a positively charged monomer copolymerises with the methacrylate anion, while in the latter the monomer polymerises with unionised methacrylic acid. The copolymers obtained are sparingly soluble in water but readily dissolve in solutions of acids. Bearing in mind that Q and e for methacrylic acid and the methacrylate ion are 2.0, +0.7 and 0.9, −1.0 respectively, the presence of the cobalt-containing group leads to a decrease of Q_1 for both monomers and also of e_1 for *cis*-dimethacrylatotetramminecobalt(III) perchlorate. It is striking that the copolymer obtained at pH 3 contained a much larger isotactic fraction.

The copolymerisation (pH 1, 323 K, inert atmosphere, $K_2S_2O_8$) of methacrylatopentamminecobalt(III) perchlorate with sodium styrene-*p*-sulphonate has also been investigated[121]. After 12–24 h, the yield of the copolymer reached 5–10%. This resulted in the formation of a polyampholyte insoluble in water, DMF, and DMSO, consisting of an alternating copolymer (A–B–A), in which the molar content of the sodium salt of styrenesulphonate was independent of the composition of the reaction mixture and amounted to 60–70%. The copolymer obtained is characterised by a repeating unit as a result of the polymerisation of a transition structure:



Evidently, because of their hydrophobic character, the formation of such structures via the ionic interaction between the monomers is more probable than the formation of pairs of ionised monomers with a counterion. Generally speaking, by virtue of the wide variation of the values of Q and e, MCM provide greater possibilities than the usual monomers for the synthesis of alternating copolymers, but this problem has not been adequately analysed for MCM based on transition metals owing to the lack of experimental data.

3. Copolymerisation of MCM Incorporating a Coordination-Saturated Metal

We shall examine two cases: when one or both copolymerising monomers form complexes with metal compounds. In the former case the copolymerisation of MMA with vinylidene chloride, 2,6-dichlorostyrene, *p*-chlorostyrene, and styrene (AIBN or ultraviolet irradiation, 323 K) in the presence of $ZnCl_2$ or $AlBr_3$ leads to the formation of alternating copolymers[59] as a consequence of the rapid increase of the effective rate constants for cross chain propagation under the influence of the complex-forming agent. According to other data[122], in the copolymerisation of styrene with methyl acrylate in the presence of $ZnCl_2$ (spontaneous process or photoinitiated), the composition of the copolymer depended on the monomer ratio; alternation was observed only when the molar content of methyl acrylate in the initial mixture was <0.8. This has been attributed to the formation of two types of complexes: $ZnCl_2$–methyl acrylate and $ZnCl_2$–methyl acrylate–styrene; accordingly, the alternating copolymer is a product of the homopolymerisation of the second complex, while in the presence of an excess of methyl acrylate in the monomer mixture the two types of complexes copolymerise. The spontaneous compolymerisation of 1,3-cyclopentadiene with acrylonitrile in the presence of $ZnCl_2$ led to the simultaneous formation of a copolymer having a predominantly 1,4-*cis*-structure and a small amount of a cyclic adduct[123].

The characteristics of the radical copolymerisation of allylbenzene with methyl acrylate, acrylonitrile, methacrylonitrile, and fumaronitrile in the presence of $ZnCl_2$, $ZnBr_2$, ZnI_2, $Zn(SCN)_2$, $AlCl_3$, or $SnCl_4$ (333 K, AIBN) have been investigated[124]. In the allylbenzene–MMA and allylbenzene–fumaronitrile systems in the absence of the above salts polymerisation did not occur, while in the presence of $ZnCl_2$ alternating copolymers were formed. The values of Q and e have been calculated for acrylonitrile and MMA bound in complexes with $ZnCl_2$.

Alternating copolymers have also been obtained in the copolymerisation of monomers each of which is capable of the formation of complexes with MX_n—for example, acrylic acid and acrylamide in the presence of $ZnCl_2$ (AIBN, 318 K, benzene)[124].

It is noteworthy that, in the copolymerisation of allyl monomers with vinyl monomers (M_1), the presence of MX_n hardly influences r_2.[59] On the other hand, in copolymerisation with monomers each of which is capable of forming a complex (allyl acetate or allyl alcohol with MMA; $ZnCl_2$, $AlBr_3$), the parameters r_1 and r_2 become appreciably closer to each other. However, as shown for the MMA–acrylonitrile and methyl acrylate–acrylonitrile pairs of monomers[36], when $SnCl_4$ is used as the complex-forming agent, the corresponding ester is more reactive regardless of the ratio of the reactivities of the initial monomers.

The copolymerisation of styrene (M_1) with vinylpyridines (DMF, AIBN, 323 K) in the presence of $CoCl_2.6H_2O$ [64] leads to a considerable (approximately threefold) increase of r_1, compared with the same process in the absence of an additive, and to just as large a decrease of r_2 (for both 4-VP and 2-VP and methylvinylpyridine). The authors[64] attribute these effects to the formation of the corresponding complexes.

The copolymers of *cis*-$[Ru(bipy)_2(4\text{-}VP)X]^{n+}$ with styrene, MMA, and 4-VP (AIBN, 343–348 K, solvent—CH_3CN) have been described[66]. The structures of the polymers have been demonstrated by elemental analysis and infrared spectroscopy.

The vinylimidazole complexes of nickel(II), cobalt(II), iron(III), and copper(II) acetates copolymerise with vinylpyrrolidinone when divinylbenzene is added as the cross-linking agent (γ-irradiation, aqueous solution)[126]. After irradiation, the resulting polymer was ground and the metal ion as a "template" was removed by boiling the polymer powder in hydrochloric acid. It was found that each "template" polymer then adsorbed metal ions more effectively than pure polyvinylimidazole. The cobalt-containing "template" polymer adsorbed Co^{2+} ions most effectively, while selective adsorption was not observed for other "template" polymers

The radical copolymerisation of a series of cobalt-, nickel-, and palladium-containing complexes of styrylphosphines with styrene in various organic solvents has been reported[129].

We may note an interesting feature of the copolymerisation of MCM in complexes with olefins. In the copolymerisation of ethylene with vinylpyridines[130], acrylonitrile[131], or MMA,[132] the metal-containing monomer bound in complexes with VCl_4, $TiCl_4$, and $VOCl_3$ functions as a component of a metal complex catalytic system, on the one hand, and the formation of complexes by these monomers prevents the inhibiting effect of the heteroatoms on the anionic-coordination polymerisation of olefins and activates the double bond in the monomers, on the other. The mechanism of this process can be represented in the following form[132]:

$$VCl_4\cdot MMA + AlR_xCl_{3-x} \rightarrow VCl_4 + MMA\cdot AlR_xCl_{3-x}$$

$$VCl_4 + AlR_xCl_{3-x} \xrightarrow{C_2H_4} \rangle V\text{—}(\text{—}CH_2CH_2\text{—})_n\text{—} +$$

$$+ CH_2{=}C(CH_3)C{=}O \rightarrow AlR_xCl_{3-x} \rightarrow \rangle V\text{—}CH_2\text{—}C(CH_3)(\text{—}CH_2\text{—}CH_2\text{—})_n\text{—}$$

$$C(O \rightarrow AlR_xCl_{3-x})(O\text{—}CH_3)$$

¶ It is of interest to note that a similar "adjustment" phenomenon was also observed in the formation of complexes of the corresponding cations with certain copolymers and subsequent cross-linking[127,128]. After the removal of ions there is in this instance an appreciable increase of sorption capacity and of the rate of sorption on the "adjusted" sorbents. However, in contrast to the study of Kato et al.[126], an increased selectivity in relation to the metal ion with respect to which the given sorbents had been "adjusted" was noted[127].

The formation of complexes of $Al(C_2H_5)_2Cl$ with polar monomers (acrylonitrile, acrylic acid, and potassium methacrylate) leads to similar results, which facilitates their copolymerisation with ethylene in the presence of the $VO(OC_2H_5)_3$–$Al(C_2H_5)_2Cl$ catalytic system[133]. The content of the polar monomer in such copolymers reaches 2.5 wt.%.

4. Copolymerisation of MCM With a π-Bonded Transition Metal

The copolymerisation of π-bonded MCM with classical vinyl monomers is apparently the most thoroughly investigated branch of the polymer chemistry of MCM. The results of the study of the copolymerisation of styrenetricarbonylchromium, η^5-vinylcyclopentadienyltricarbonylmanganese, η^6-(2-phenylalkyl acrylates)tricarbonylchromium, and η^4-(hexa-2,4-dien-1-yl acrylate)tricarbonyl with styrene, vinyl acetate, acrylonitrile, MMA, butadiene, and other monomers have been summarised in review[1,84]. Methylvinylcyclopentadienyltricarbonylmanganese (the 1,2- and 1,3-isomers) was copolymerised[109] with styrene and 1,4-divinylbenzene; the products contained 27–50 mole % of MCM.

Two studies were devoted to problems of the copolymerisation of η^5-vinylcyclopentadienyltricarbonylmethyltungsten, η^5-vinylcyclopentadienyldicarbonylnitrosyl molybdenum, η^5-vinylcyclopentadienyldicarbonylnitrosylchromium, η^5-vinylcyclopentadienyldicarbonylnitrosyliridium, vinylruthenocene, and vinylosmocene[85,90]. Data on the copolymerisation parameters and the values of Q and e for the MCM considered are listed in Table 4. The copolymerisation of MCM with π-bonded metal is characterised by large negative values of e (from −1.6 to −2.1), which is associated with the powerful electron-donating character of the cyclopentadienyl ring and the conclusion[85] that the nature of the metal, the addition of the NO group and the two CO groups have little influence on the reactivity of the monomers is apparently quite justifiable.

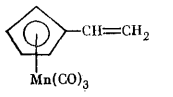
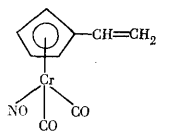
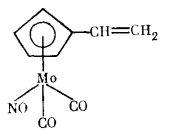
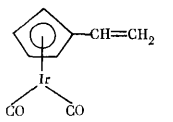
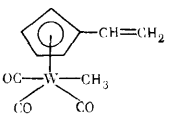
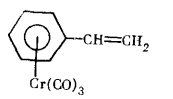
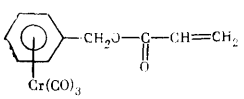
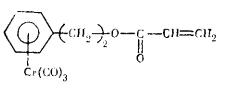
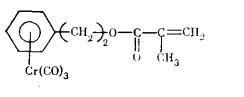
We may note also that $r_1 = 0$ has been obtained for the radical copolymerisation of tricarbonylstyrenechromium (M_1) with styrene or MMA,[134] i.e. the growing chain terminating in the M_1 group cannot combine with M_1, which is consistent with the inability of styrenetricarbonylchromium to undergo homopolymerisation.

A characteristic feature of the copolymerisation of η^6-(2-phenylethyl acrylate)tricarbonylchromium with styrene, MMA, and acrylic acid is the formation of polymers with a broad bimodal molecular weight distribution: MW > 10^6 for the high-molecular-weight fraction and 1×10^4–6×10^4 for the low-molecular-weight fraction. The high-molecular-weight fraction consists of a highly branched polymer, which is also observed with copolymers of η^4-(hexa-2,4-dien-1-yl acrylate)-tricarbonyliron copolymers. The copolymer containing 28 mole % of MCM has been obtained by the copolymerisation of 3-vinylbisfulvalenedi-iron with styrene (monomer ratio 1 : 4).[88] Its treatment with TCNQ in benzene, $CHCl_3$, or benzonitrile led to the oxidation of 88% of the initial amount of iron(II) and the formation of the mixed-valence salts $[Fe^{II}\text{—}Fe^{III}][TCNQ]_2^-$ analogous to homopolymer salts. However, their conductivity (2.5×10^{-5} Ω^{-1} cm^{-1}) was lower than for the homopolymer salts [$(6 - 9) \times 10^{-3}$ Ω^{-1} cm^{-1}].

5. Copolymerisation of Various MCM With One Another

Studies of the copolymerisation of various MCM in order to obtain bimetallic metal-containing polymers have been extremely limited although such products might apparently be of definite interest (for example, in metal complex catalysis).

Table 4. The copolymerisation constants and the parameters Q and e for the copolymerisation of π-bonded MCM*.

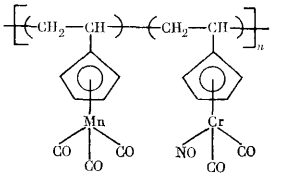
Monomer M_1	Parameter	Styrene	MA	MMA	AN	VA	Refs.
	r_1	0.10	—	0.19	2.35	0.19	[137]
	r_2	2.5	—	0.47	0.06	0.22	
	Q	1.03	—	—	—	—	
	e	−1.99	—	−0.95	−0.59	−2.9	
	r_1	0.30	—	—	—	5.3	[138]
	r_2	0.82	—	—	—	0.079	
	Q	3.13	—	—	—	—	
	e	−1.98	—	—	—	—	
	r_1	0.31	—	—	—	—	[85]
	r_2	0.83	—	—	—	—	
	Q	—	—	—	—	—	
	e	−1.97	—	—	—	—	
	r_1	0.29	—	—	—	—	[85]
	r_2	0.77	—	—	—	—	
	Q	—	—	—	—	—	
	e	—	—	—	—	—	
	r_1	0.16	—	—	—	—	[89, 91]
	r_2	1.55	—	—	—	—	
	Q	1.66	—	—	—	—	
	e	−1.98	—	—	—	—	
	r_1	0	—	0	—	—	[134]
	r_2	1.39	—	0.75	—	—	
	Q	—	—	—	—	—	
	e	—	—	—	—	—	
	r_1	0.10	0.56	—	—	—	[84]
	r_2	0.34	0.62	—	—	—	
	Q	—	—	—	—	—	
	e	—	—	—	—	—	
	r_1	0.1	0.3	—	0.6	—	[135]
	r_2	0.5	1.0	—	0.2	—	
	Q	—	—	—	—	—	
	e	—	—	—	—	—	
	r_1	0.04	—	0.90	0.07	—	[136]
	r_2	1.35	—	1.19	0.79	—	
	Q	—	—	—	—	—	
	e	—	—	—	—	—	

*For the notation, see Table 1.

Among the most significant advances in this field we may mention the copolymerisation of vinylcyclopentadienyltricarbonylmanganese with vinylferrocene (benzene, 343 K, AIBN), for which $r_1 = 0.44$, $r_2 = 0.49$, $e_1 = -2.6$, and $e_2 = -2.1$, while the polymer obtained had $\bar{M}_n = 7700$ and $\bar{M}_w = 13800$.[137]

The radical copolymerisation of η^6-(benzyl acrylate)tricarbonylchromium with ferrocenylethyl acrylate takes place readily in ethyl acetate[1].

The polymer having the structure



was obtained only for a specific ratio of the monomers, i.e. η^5-vinylcyclopentadienyltricarbonylmanganese and η^5-vinylcyclopentadienyldicarbonylnitrosylchromium[138].

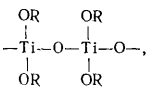
The copopolymerisation of two monomers incorporating iron and zinc methacrylates together with unsubstituted methacrylic acid had been reported[139]. It has been suggested that a long-range interaction transmitted via the polymer chain takes place between the iron and zinc atoms.

The copolymerisation of different MCM is not the only method of synthesis of bimetallic polymers. For this purpose, one can also use polycondensation methods (see below) and methods involving the polymerisation of bimetallic monomers for which there are virtually no experimental data, as mentioned above. However, an attempt has been made[140] to combine clusters with traditional monomers and to polymerise and copolymerise them. This method is believed to be promising although its application is complicated by the reactions of the initiator with the cluster and also by the large differences between the relative reactivities of the monomers in clusters and the traditional monomers.

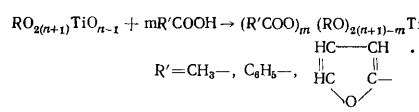
Thus the copolymerisation of MCM with traditional monomers makes it possible to determine the influence of the nature of the metal in the MCM on the relative reactivities of the copolymerising monomers. Although this influence is difficult to treat systematically owing to specific factors even in MCM-homologues, nevertheless allowance for it makes it possible in many instances to act effectively on the copolymerisation process and on the properties of the products formed (see Section VIII).

V. POLYMERISATION AND COPOLYMERISATION OF OLIGOMERIC METAL-CONTAINING MONOMERS

Metal-containing oligomers as well as polymers incorporating multiple bonds are capable of polymerisation and copolymerisation. Oligomeric MCM are frequently formed already in the stage involving the synthesis of the monomers as the main or side products. Only the homopolymerisation of titanium-containing polymers of the type



in which some of the surrounding groups are unsaturated, and their copolymerisation with vinyl monomers have been investigated. Such compounds have been obtained by polymer-analogue reactions based on the ease of substitution of the alkoxy-groups in polyalkoxytitanoxanes by acyl residues with multiple bonds[7,49,141]:



Thus the interaction between polybutoxytitanoxane and

methacrylic as well as furylacrylic and cinnamic acids leads to the formation of waxy or rosin-like substances (depending on the amount of acid introduced). Polybutoxytitanoxane methacrylate behaved analogously to its low-molecular-weight analogue—tributoxytitanium methacrylate—because in the presence of bonzyl peroxide polymerisation did not take place even after prolonged heating, while on initiation with AIBN and heating at 423 K for 5 h there was an appreciable decrease of the number of double bonds[49]. Polybutoxytitanoxane furylacrylate and polybutoxytitanoxane cinnamate copolymerise with styrene (373 K, 1–2% of benzoyl peroxide); transparent red-brown copolymers are formed; in contrast to the initial polybutoxytitanoxane, they proved to be insoluble in solvents such as acetone, benzene, and toluene and did not react even with boiling water. Similar reactions have not been described for oligomeric products containing other metals. Here we may also mention the oligomeric π-complexes of tungsten[201] obtained by exchange reactions.

VI. GRAFT POLYMERISATION

There are few data concerning the graft polymerisation of MCM and almost all the publications on this question have appeared only in the last ten years. Only the results of studies on the radical graft polymerisation of MCM have been described and chemical initiation methods have been usually employed. MCM based on non-transition metal salts of acrylic acid have been largely used for grafting, evidently due to the ease of their synthesis and ready polymerisability.

Thus the $(NH_4)_2S_2O_6$–$Na_2S_2O_3$ oxidation-reduction system[142] proved to be effective for the grafting of sodium acrylate to a polysaccharide and $(NH_4)_2S_2O_8$ was effective in the grafting of sodium acrylate and methacrylate to cellulose[143]. An interesting method for the grafting of acrylate and sodium ethylenesulphonate has been proposed[144]. Wool fibre was kept in an aqueous solution of the MCM after which it was treated with a gas discharge plasma, the yield of the graft copolymer reaching 2–5%. This method is extremely promising and can apparently be extended also to other MCM. The method of chemical initiation (by the Fe^{2+}–H_2O_2 oxidation-reduction system) has been used[145] also for the grafting of calcium acrylate to cellulose in aqueous solution. When a 20% solution was employed, the process took place at a high rate and terminated after 5 min. An increase of temperature from 292 to 353 K did not affect the yield of the graft copolymer, while a decrease of the MCM concentration to 16% sharply reduced it. Evidently, when 20–30% aqueous solutions of calcium acrylate are used, associated monomer species with an ordered molecular arrangement are involved in the grafting.

The grafting of zinc acrylate to polyolefins[146] and of the calcium and barium salts of acrylic and methacrylic acids to polypropylene and poly(vinyl chloride) fibres[147,148] has been reported.

However, the use of chemical grafting methods should lead to the formation of considerable amounts of the homopolymer together with the graft copolymer. The application of high-energy radiation (the radiation from the ^{60}Co isotope, an electron accelerator, and a glow discharge plasma) as the initiator of graft postpolymerisation has considerable advantages in this respect. The attempts at direct post-irradiation (accelerated electrons) grafting of sodium methylene- and styrene-sulphonates to a polyethylene film were unsuccessful[200]. On the other hand, these monomers were grafted after the preliminary hydrolysis of polyethylene.

The trapped radical method, involving contact between the grafting solution and a polymer support subjected to preliminary irradiation *in vacuo* has been used for the grafting of certain titanium- and vanadium-containing monomers to powdered polyethylene, polypropylene, polystyrene, and the ethylene–propene copolymer[149,150]. MCM of both acrylic and allylic series have been used. When $(C_5H_5)_2Ti(Cl).OCH_2CH{=}CH_2$, $(C_4H_9O)_2Ti[NH(CH_2CH{=}CH_2)]_2$, $Cl_3Ti(OCH_2.CH{=}CH_2)$, $(C_3H_7O)_3Ti(OCH_2CH{=}CH_2)$, and $CH_2{=}CHCH_2.OVOCl_2$ were grafted, the metal content in the graft copolymer did not exceed 0.10–0.12%, which is not surprising bearing in mind the low tendency of allylic compound towards polymerisation.

On the other hand, in the radiation-induced graft postpolymerisation of tributoxytitanium acrylate (preliminary irradiation dose *in vacuo* 200 kJ kg^{-1}) the maximum metal content also did not exceed the values quoted above[151]. This is apparently due to the steric hindrance to the chain propagation reaction associated with the large size of the $Ti(OC_4H_9)_3$ group. In the study of the temperature variation of the yield of the grafting process, a maximum was found in the region of 303 K, which can be accounted for by the superposition of two competing effects: the increase of the rate of chain propagation and the increase of the rate of destruction of the polymeric radicals with increase of temperature.

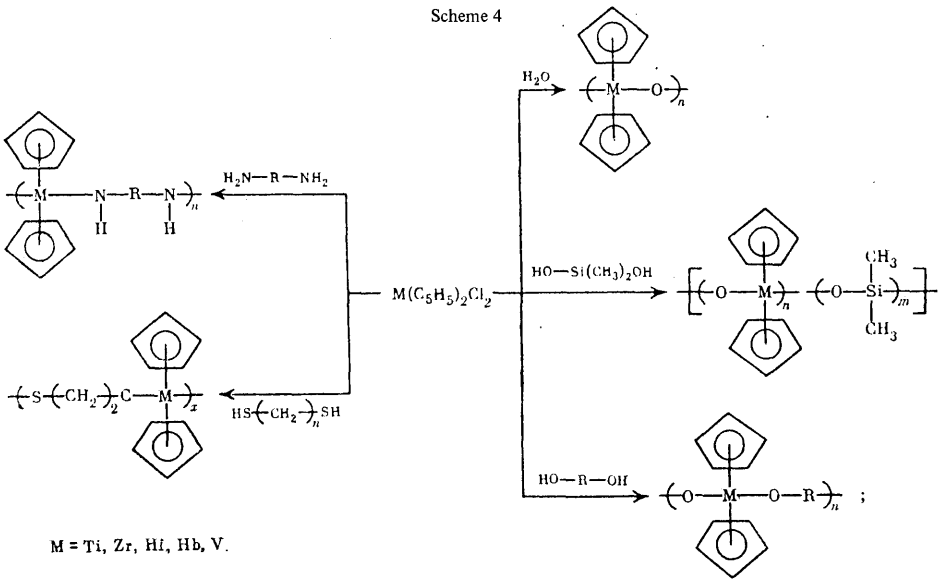
The grafting of monomers bound in complexes is an extremely promising branch of the graft polymerisation of MCM. The addition of the $ZnCl_2$, ZnI_2, or $AlCl_3$ salts proved to have an insignificant influence on the graft polymerisation of arcrylamide, MMA vinyl acetate, and styrene on 1,4-polybutadiene (benzene, 333 K, AIBN).[152] On the other hand, the grafting of MMA or styrene to 1,2-polybutadiene was greatly accelerated in the presence of these salts, which can be arranged in the following sequence in terms of their influence on the grafting parameters: $ZnCl_2 > AlCl_3 > ZnI_2$. The case considered is the only example illustrating the role of the steric structure of the polymeric support on the character of the grafting of MCM.

The possibility of grafting the complex of an organic or inorganic nickel salt with vinylpyridine (molar ratio from 0.1 : 1 to 1 : 1) to rubber in the presence of a radical initiator has been demonstrated[153].

All that has been said above concerning the polymerisation of allylic monomers bound in complexes holds also for their graft polymerisation. Allyl alcohol, allylamine, allyl acetate, allylmercaptan, etc. have been grafted to polyethylene, polypropylene, polystyrene, and poly(methyl methacrylate) in the presence of LiCl, CaCl, and $ZnCl_2$.[154,155] The method of joint irradiation has been used for this purpose. The rate of the graft polymerisation of allyl alcohol (AAl) increased by a factor of 5 for the molar ratio $[AAl] : [ZnCl_2] = 2 : 1$.[155] The graft copolymers of certain other allylic monomers have been obtained for the first time[154]. In addition, after the attainment of the same degree of grafting of vinyl monomers, the necessary irradiation dose increased considerably (by a factor greater than four).

The graft polymerisation of allylic monomers in the presence of certain transition metal salts has also been achieved. Allyl alcohol, allylamine, and diallylamine have been grafted to powdered polyethylene and polypropylene by the method of post-irradiation graft polymerisation (preliminary irradiation both *in vacuo* and in air) in the presence of $CoCl_2$, $Co(NO_3)_2.6H_2O$, NiI_2, and $CrCl_3.6H_2O$.[156] In the grafting of the complex $CoCl_2(AAl)$ (the dose in the preliminary irradiation of polyethylene in air was 200 kJ kg^{-1}; molar ratio $AAl : CoCl_2 = 3 : 1$, 343 K, inert atmosphere) the rate of the process is constant over a considerable time interval, as shown by the linear relation between the cobalt content in the copolymer and the reaction time. The activation energy for this process has been calculated as 40 kJ mol^{-1}. This procedure can probably be used also for the graft copolymerisation of MCM

Scheme 4



probably be used also for the graft copolymerisation of MCM with vinyl or allyl monomers and possibly also heterometallic MCM. There are no data concerning the graft polymerisation of π-bonded MCM.

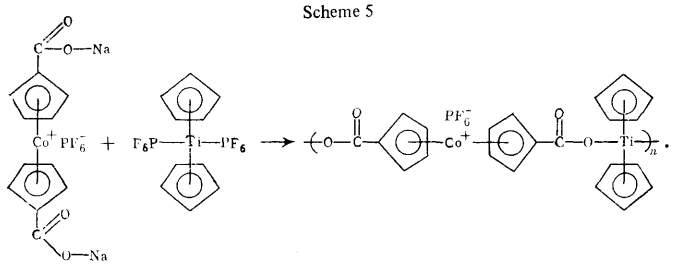
VII. POLYCONDENSATION REACTIONS OF METAL-CONTAINING COMPOUNDS

The condensation of metallocene compounds has been studied in fair detail; the comparatively early studies have been surveyed by Korshak[7] and Neuse and Rosenberg[157], while reviews of later work can be found in a number of other publications[158–164,203–205]. Reactions of this kind are presented in a general form in Scheme 4.

The degree of polycondensation in such products varies within wide limits—from 2 to 2000 depending on the nature of the reactants. A convenient method for the preparation of metallocene polymers by reaction with aldehydes has been described[165].

Polycondensation reactions of metallocenes, for example, between cobaltocene derivatives and titanocene[158] (Scheme 5), leading to the formation of a polymer chain incorporating different transition metal atoms, are known:

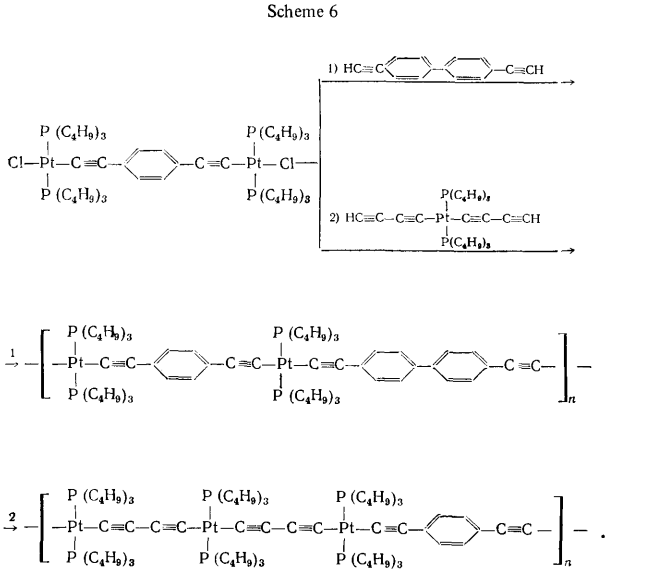
Scheme 5



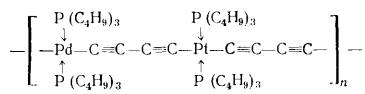
Many of the reactions considered will probably prove to be promising for the synthesis of polymers based not only on metallocene derivatives but also on alkoxy-, amido-, amino-, and carboxy-derivatives of transition metals. For example, linear conjugated coordination polymers have been obtained by the condensation of tetrakis(salicylhaldehydo)zirconium(IV) with 1,2,4,5-tetra-aminobenzene or dicarboxybis(5,7-dichloro-8-quinolato)(triphenylphosphine)tungsten with quinoline-5,8-diol.[166] The molecular weight of the polymers reaches 50000 and their characteristic feature is the inclusion of octacoordinate metals. The formation of similar products can be expected also for molybdenum, niobium, rhenium, etc.; vigorous researches are being prosecuted on these lines.

An interesting series of studies[167–174] has been devoted to the polycondensation of acetylenic MCM. In the presence of copper(I) iodide or chloride, such MCM are capable of forming polymers with chloro-derivatives of nickel, palladium, and platinum and some can undergo copolycondensation with diethynylbenzene. A wide variety of poly-yne polymers containing nickel, palladium, or platinum atoms in the main chain have been synthesised in this way (Scheme 6).

Scheme 6



The poly-yne polymers are soluble in various organic solvents despite the fact that they possess a rigid rod-like structure in solution. Polymers containing different metals in the main chain, for example palladium and platinum, have been obtained in the same way[170]:



These polymers had molecular weights ranging from 8000 to 120000 and under certain conditions they depolymerised with formation of polynuclear complexes with a Pt–C bond. It is striking that in all cases the products formed can be regarded as alternating copolymers. The characteristic features of the polycondensation of acetylenic derivatives of the ferrocene type have been surveyed in a recent review[175].

VIII. APPLICATIONS OF METAL-CONTAINING POLYMERS

Metal-containing polymers are finding a wide variety of applications which are sometimes unexpected; such data have been published mainly in the patent literature. It is possible to note two main trends: applications involving the improvement of some properties of polymers and compositions based on them and applications based on the appearance of new properties due to the presence of the metal in the main or side chain of the polymer.

Thus the introduction of lithium, sodium, or potassium methacrylate units into PMMA greatly increases the thermal-stability of the polymer and to a greater extent for shorter PMMA blocks[176]. Intramolecular cyclisation reactions involving neighbouring side groups take place in this instance with formation of anhydride rings and the corresponding metal methoxide. The introduction of sodium methylallenesulphonate into polyacrylonitrile has an appreciable influence on the glass point (T_g) of the copolymer[177]: a relation with a maximum corresponding to an MCM content in the copolymer of 8 wt.% was observed. The increase of T_g is apparently associated with the increase of the rigidity of the chain as a result of the incorporation in the latter of more bulky polar groups. With high MCM contents, the intermolecular interaction of the nitrile groups weakens as a consequence of the loosening of the structure.

The addition of sodium or zinc polyacrylate to certain compositions[178] greatly increases their heat resistance and resistance to a corona discharge; the copolymers of sodium or potassium acrylate with unsaturated polyesters have a high impact strength, dimensional stability, and fire resistance[179]. The styrene–methacrylic acid–sodium methacrylate ternary copolymer is characterised by an increased yield point, which has been attributed[180] to an increased degree of neutralisation of the carboxy-groups. Titanium-containing polymers exhibit properties known as "anomalous fibre formation"[90]; their mass and initial dimensions change little under the conditions of heat treatment.

All the polymers based on MCM incorporating transition metals are as a rule stable up to 473–523 K. Even their low content in copolymers with traditional monomers, for example, those of zirconyl acrylate or methacrylate with alkyl acrylates[53], leads to the formation of a cross-linked polymer with enhanced thermoplastic properties and improved resistance to organic solvents. These properties are used, especially in the case of titanium-containing polymers, to obtain various coatings, frequently with enamel-like surfaces. We may also note the application of metal-containing polymers, obtained by the polymerisation or copolymerisation of MCM, as the main components in the preparation of foam plastics[181], hydrophilic finishing preparations for crease-resistant cotton fabrics[182], and as materials with effective slip[183]. Alkaline earth metal and copper acrylates and methacrylates are used as the principal components in the preparation of soil structure-forming agents designed for the stabilisation of soils[184–186], as water isolating agents in the recovery of petroleum[187], and as flocculants and coagulants[188,189].

One of the most promising applications of metal-containing polymers is their use as metal complex catalysts in numerous processes. Thus polymers obtained by the polymerisation of styrylphosphines bound in complexes with cobalt, nickel, and palladium salts catalyse hydroformylation reactions[129], while ferrocene-containing polymers catalyse dehydrogenation and dehydration processes[175].

As was to be expected, metal-containing graft polymers proved to be even more effective catalysts: for example, the grafted complexes of nickel salts with vinylpyridine on natural rubber catalyse the dimerisation of ethylene[153]; titanium- and vanadium-containing monomers grafted on powdered polyolefins catalyse the polymerisation and copolymerisation of ethylene[150]. The complex of $PdCl_2$ with 4-vinylpyridine grafted on the surface of ethylene proved to be an effective catalyst of the stereospecific polymerisation of acetylenic monomers[190,191] and also of the reductive *N*-alkylation of nitrobenzene and its reudction products by carbonyl compounds[192]. Data concerning the possibility of employing polymerisation, copolymerisation, and graft polymerisation processes involving MCM for the preparation of deposited catalysts to be used in various processes have been summarised in two communications[193,194]. The fixation of molecular nitrogen by manganese-containing metallopolymers has been reported[199]. Metal-containing polymers based on lead and tungsten metallocene monomers have been used as coatings for targets in laser-induced thermonuclear synthesis[202].

Many metal-containing polymers have bactericidal properties. Platinum-containing condensation polymers have been used in the treatment of tumours[195], the platinum complex being slowly split off in the course of biochemical hydrolysis, which leads to prolonged action of this drug. Polymers of η^5-vinylcyclopentadienyltricarbonylmanganese and its copolymers are used as inhibitors of fungal growth[137]. Germanium-containing polymers are employed in the treatment of fibrosis of the lungs[196].

The potential applications of metal-containing polymers in this field have not yet been fully investigated. The consideration of metal-containing polymers for the purpose of imparting specific operational properties to the compositions formed merits attention. This concerns the application of Group I–IV metal acrylate and methacrylate polymers as well as their copolymers with vinyl monomers as thermostabilisers for chlorine-containing resins, for example poly(vinyl chloride)[206–208].

The method of stabilisation of such polymers at the stage of their synthesis, for example, by the copolymerisation of tin-containing monomers with vinyl chloride, is of special interest[19]. In this case the stabilising centres in the copolymer are distributed in a sequence determined by the copolymerisation parameters and are not removed from the polymer during its use (constitutionally stabilised polymers). Stable and uniform constitutional colouring of polyolefins, based on the use as cocatalyst of the product of the interaction of titanium(IV), vanadium(III), and vanadium(V) with diazoacetylenic alcohols containing a multiple bond and a chromophoric group, was achieved by similar method[209].

On the other hand, thermal and photochemical degradation of a metal-containing polymer can result in the formation of metals or their oxides, which leads in the first place to the

generation of systems with new properties. Thus ultraviolet irradiation of films of the η^6-(2-phenylethyl acrylate)tricarbonylchromium–styrene copolymer was accompanied by the elimination of a CO group and the formation of Cr_2O_3 incorporated in cross-linked films[135]. This also applies to polymers obtained by the polymerisation of monomers containing iron[210]. The decomposition of certain polymers to the oxide takes place only at temperatures above 1000 K.

Among other applications of metal-containing polymers, one may name the formation of light-sensitive media for photocopying devices, adhesives, combustion moderators, flame extinguishers, electrically conducting materials[88] and semiconductors, and ion exchangers. The products of the polymerisation and polycondensation of MCM have been used as photosensitisers and materials for protection against heat and radiation. Photopolymerisation systems for the rapid dry production of an image have been developed and investigated. Barium acrylate has been used as their main component[211,212]. The radical copolymerisation of MMA with palladium, calcium, barium, and strontium methacrylates has been carried out to prepare photoresistors with a high sensitivity and a satisfactory resolving power, which are resistant to the action of high temperatures and corrosive media[213].

The applications of metal-containing polymers are apparently not restricted to these fields. Their considerable expansion may be expected, since the synthetic possibilities in this rapidly developing branch of polymer chemistry have not been fully elucidated as yet and have been by no means completely realised.

At the same time this field of study involves a whole series of problems whose solutions will make it possible to discover general characteristics. We believe that the most important of these are as follows: the search for methods of stabilisation of MCM (especially organometallic MCM), the synthesis of bimetallic and polymetallic MCM; the development of methods for the effective activation of the multiple bonds in MCM, new methods for the initiation of polymerisation processes, and a detailed analysis of the influence of the nature of the metal on the elementary stages of the polymerisation process; problems of the stereoregulation and supermolecular organisation of metal-containing polymers; characteristic features of the alternating copolymerisation of MCM with one another and with traditional monomers; the study of the structure of the chains of metallopolymers, the changes undergone by metals following their incorporation in the polymer matrix, and also the cooperative interaction between metal atoms; problems of catalysis and the elucidation of specific features of the chain structure of metal complexes and its manifestation in catalytic processes; the study of the reactivity of the multiple bonds in MCM in other reactions involving these bonds. Only the hydrogenation of monomers bound in complexes, whose rate, as in the case of polymerisation, is higher than in the absence of a complex-forming agent, has been investigated on these lines[214,215].

Although the analysis of the results of the study of the polymerisation and copolymerisation processes involving MCM indicates a considerable progress in the understanding of many aspects of this problem and also the intensity of the studies in this field, the elucidation of fairly general characteristics of these processes requires concerted studies by chemists specialising in the field of organometallic synthesis and in polymer chemistry.

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Fluorine-containing Dyes

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The methods of synthesis, properties, and applications of fluorine-containing dyes of all classes are examined. The influence of fluorine atoms and fluorinated substituents on the spectroscopic properties of dyes is discussed. It is shown that the introduction of fluorine-containing substituents makes it possible to obtain dyes which are resistant to oxidation, light, and other physical influences.
The bibliography includes 271 references.

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I. INTRODUCTION

The vigorous development of the chemistry of organofluorine compounds and the development of convenient methods for their synthesis[1-7] have made it possible to introduce fluorine atoms and fluorine-containing substituents into the molecules of various organic substances and hence to modify their properties within wide limits. Representatives of all classes of organic dyes with fluorine-containing substituents have now been synthesised. The influence of these substituents on the colour and other properties of the dyes has been investigated and dyes with properties of practical values have been discovered.

This review deals mainly with dyes which make it possible to elucidate the influence of fluorine-containing substituents on their colour and properties. Consideration of the available data will help in the development of a theory of the colour of organic dyes, in the expansion of experimental research in this field, and in the practical utilisation of fluorine-containing dyes.

The review covers the literature up to 1981 inclusive.

II. POLYMETHINE DYES

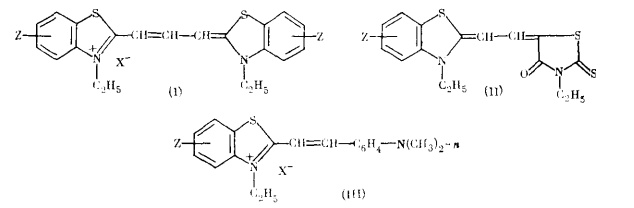
Fluorine-containing cyanine dyes were first synthesised by Kiprianov and Yagupol'skii in 1950.[8] Since then numerous communications dealing with the study of the influence of fluorine atoms and fluorine-containing substituents on the absorption spectra of dyes and their properties have been published. Some fluorine-containing-dyes have found important practical applications as cinefilm photosensitisers.

1. Dyes with Fluorine-containing Substituents in Heterocyclic Nuclei

The influence of fluorine atoms and fluorine-containing substituents in heterocyclic nuclei on the absorption spectra has been studied in detail in relation to benzothiazole derivatives—thiacarbocyanines (I), merocyanines (II), and styryl dyes (III) (Table 1).

Fluorine atoms and fluorine-containing substituents have been introduced into heterocyclic nuclei by methods dealt with in monographs and reviews[1-7]. The dyes (I)–(V) (Tables 1 and 2) were synthesised from the quaternary salts of substituted heterocyclic bases by the usual methods of the chemistry of cyanine dyes.

Table 1. The absorption maxima of dyes (I)–(III) in ethanol.



Z	Dye (I)		Dye (II)		Dye (III)	
	λ, nm	Δλ	λ, nm	Δλ	λ, nm	Δλ
H	558	—	524 [9]	—	530 [8]	—
5-F	562 [9]	4	—	—	—	—
6-F	558 [8]	0	—	—	543 [8]	4
5-CF_3	557 [9]	−1	—	—	540 [9]	10
6-CF_3	561 [10]	3	—	—	548 [10]	18
5,6-$(CF_3)_2$	557 [11]	−1	—	—	—	—
6-CH=$CHCF_3$	582 [12]	24	530 [12]	6	550 [12]	20
6-CF=$CFCF_3$	579 [12]	21	525 [12]	1	556 [12]	26
5-OCF_3	561 [13]	3	—	—	545 [13]	15
6-OCF_3	560 [13]	2	—	—	540 [13]	10
5-SCF_3	560 [14, 15]	2	—	—	543 [13]	13
6-SCF_3	568 [15]	10	—	—	540 [14]	10
5-SO_2CF_3	556 [16]	−2	505 [10]	−19	555 [16]	25
6-SO_2CF_3	575 [10]	17	513 [10]	−11	566 [10]	36
6-$SeCF_3$	570 [17]	12	522 [17]	−2	549 [17]	19
5-$NHCOCF_3$	573 [18]	15	526 [18]	2	—	—
6-$NHCOCF_3$	580 [18]	22	532 [18]	8	—	—
5-$NHSO_2CF_3$	562 [18]	4	—	—	—	—
6-$NHSO_2CF_3$	565 [18]	7	—	—	—	—

Note. Here and in the other Tables the numbers in square brackets denote references (Ed.of Translation).

Monomethine di- and tri-carbothiacyanine dyes with the 6-F,[8] 5-CF_3,[9] 5-SCF_3,[15] and 6-SCF_3 [15] substituents, pentacarbothiacarbocyanines with the 5-CF_3, 6-CF_3, and 5-SO_2CF_3 substituents[19], thiacarbocyanines containing methyl and ethyl groups in the β-position in the chain and the 5-F or 6-F,[8,9]

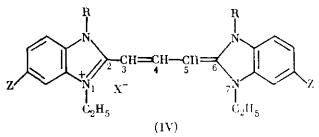
5-CF_3,[9] 5 or 6-OCF_3,[13] 5- or 6-SCF_3,[15] 5- or 6-$NHCOCF_3$,[18] and 6-$SeCF_3$ [17] substituents in the nuclei, and dyes with a condensed 2-trifluoromethyloxazole ring in the 4,5-positions[20] have also been described. Certain asymmetric dyes[8,9,14,15,21,22] as well as thiacarbocyanines with two substituents in the nuclei [5-OCF_3 and 6-X (X = Cl, I, SCH_3, NH_2, or $NHCOCH_3$) [23] and 5,6-OCF_2O [24]] are known.

Fluorine atoms in benzothiazole nuclei have little influence on the absorption spectra of dyes but reduce their basicity[25] and lower the electron-donating capacity[26] (the Brooker basicity[27]) of the heterocyclic residues. The electron-donating capacity of the benzothiazole residues is reduced to an even greater extent under the influence of the electron-accepting substituents CF_3, OCF_3, SCF_3, SO_2CF_3, $NHCOCF_3$, and $NHSO_2CF_3$, which have positive σ_n constants[28]. As a result of this, the electronic asymmetry and the deviation in styryl dyes are reduced, while in merocyanines they are enhanced[26]. Fluorine-containing substituents in styryl dyes and merocyanines give rise respectively to greater and smaller bathochromic or hypsochromic effects than in the symmetrical carbocyanines.

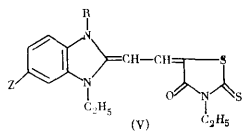
For the dyes (I) substituted in the 6,6′-positions, a correlation has been found between their basicity (pK_a) and the σ_n constants of the substituents[25,29].

Table 2 presents the spectroscopic data for the benzimidazole dyes (IV) and (V).

Table 2. The absorption maxima of dyes (IV) and (V) in ethanol.



(IV)



(V)

R	Z	Dye (IV)		Dye (V)	
		λ, nm	Δλ	λ, nm	Δλ
C_2H_5	H	498 [30]	—	514 [30]	—
C_2H_5	F	502 [30, 31]	4	515 [31]	1
C_2H_5	CF_3	501 [32]	3	515 [30]	1
C_2H_5	$C(CF_3)_3$	504 [33]	6	514 [33]	0
C_2H_5	OCF_3	502 [31]	4	518 [31]	4
C_2H_5	SCF_3	511 [17, 31]	13	520 [30, 31]	6
C_2H_5	$SeCF_3$	510 [17]	12	520 [17]	6
C_2H_5	$SOCF_3$	516 [31, 34]	18	520 [29, 35]	6
C_2H_5	SO_2CF_3	522 [30, 32]	24	524 [30, 31]	10
C_2H_5	SO_2CHF_2	515 [36]	17	519 [36]	5
C_2H_5	$SO_2C_3F_7$	525 [35]	27	525 [37]	11
C_2H_5	$SO_2CF(CF_3)_2$	526 [37]	28	525 [37]	11
C_2H_5	$SO_2C(CF_3)_3$	528 [37]	30	525 [37]	11
C_2H_5	$N(CF_3)_2$	502 [18]	4	514 [18]	0
C_6H_5	H	508 [30, 38]	—	518 [38]	—
C_6H_5	F	512 [31]	4	— —	—
C_6H_5	CF_3	511 [32]	3	511 [32]	−8
C_6H_5	SCF_3	517 [35]	9	520 [35]	1
C_6H_5	$SOCF_3$	520 [35]	12	520 [35]	1
C_6H_5	SO_2CF_3	525 [32]	17	—	—
CF_2CHF_2	H	511 [39, 40]	—	—	—

Dyes of types (IV) and (V) containing the $SO_2CF_2CHF_2$, SO_2CF_2CHClF, $SO_2CF_2CHFCF_3$,[41] $SO_2CH_2CO_2CF_3$,[34] CH=CH–CF_3,[12] CF=CF–CF,[12,30] and N=N–CF_3 [18] substituents in the nuclei and the CF_3CHClF, CF_2CHFCF_3,[39,40] $C_6H_4SO_2.CF_3$-*p*, $C_6H_4CF_3$-*m* [42] substituents at the nitrogen atoms, dyes with two substituents in the 5,6-positions (F,F;[31] CF_3, $COOCH_3$;[38] CF_2OCF_2;[31] OCF_3, Cl;[30] SO_2CF_3, Cl;[30] SO_2CF_3, OCH_3;[30] CF_3, CN [44,45]) and the 5,7-positions (SO_2CF_3, Cl;[43] CF_3, CF_3 [43]), styryl dyes with the CF=CClF or CF=$CFCF_3$ substituents at the nitrogen atom of the benzimidazole ring[40,46], imidadicarbocyanines and imidatricarbocyanines with the SO_2CF_3 groups in the nuclei[35,47], imidacarbocyanines with two chlorine atoms and the CF_3 and SO_2CF_3 groups in the nucleus and the $(CH_2)_nCF_3$ (n = 1–3) group at the nitrogen atom[39,40,48], certain asymmetric dyes with the benzimidazole nucleus containing the CF_3 [22,49] and SO_2CF_3 [50] substituents, imidadicarbocyanine with the SO_2CF_3 substituent in the nucleus and a chlorine atom in the γ-position in the chain[51], and dyes of types (IV) and (V) in which all the hydrogen atoms in the benzene ring have been substituted by fluorine atoms[52] have also been described.

Fluorine-containing substituents are electron acceptors and, after the introduction into the benzene rings of symmetrical imidacarbocyanines (IV), give rise to a bathochromic effect [from 3–4 nm for the fluorine atoms and CF_3 groups to 25–30 nm for the most electron-accepting SO_2CF_3 and SO_2C.$(CF_3)_3$ groups]. The spectroscopic effects of the substituents are then as a rule greater than in the analogous dyes of the benzothiazole series.

The bathochromic effect of electron-accepting substituents in the series of benzimidazole dyes can be explained not only by an increase in the length of the chromophoric system but also apparently by the fact that the conjugation of the substituent with one of the nitrogen atoms of the benzimidazole ring increases the hypsochromic influence of this atom as an electron-donating substituent in the polymethine chain. According to the Förster–Knott–Dewar rule[53,54] (the FKD rule), electron-donating substituents in the even positions of the polymethine chromophore [see the numbering of the atoms in formula (IV)] have a hypsochromic effect on the colour of the dye while electron-accepting substituents have a bathochromic effect. The blue shift of the colour of imidacarbocyanines (IV) compared with the thiacarbocyanines (I) can be explained by the hypsochromic influence of the nitrogen atoms. The introduction of phenyl or polyfluoroalkyl groups (R = C_6H_5, CF_2CHF, etc.) at the nitrogen atoms of the dyes (IV) diminishes the electron-donating hypsochromic influence of the nitrogen atoms and induces a red shift of the colour than for R = C_2H_5.

Fluorine-containing substituents in benzimidazole nuclei as a rule reduce the basicity of the corresponding dyes[25,29] and a correlation is observed between the pK_a and the σ_n constants of the substituents in the nuclei[29].

For dyes containing two substituents in the nucleus, the spectroscopic effects and the pK_a are approximately additive[56,57], but, when steric hindrance displaces one of the substituents from the plane of the benzene ring, the influence of the latter on pK_a and λ_{max} diminishes[57,58].

Linear correlations between the absorption frequencies of the carbonyl groups and the σ_n constants of the substituents in the nuclei have been found for the merocyanine dyes (III) and (V).[59]

The introduction of electron-accepting substituents into the imidacarbocyanine molecule improves its sensitising properties[60]. Among imidacarbocyanines with fluorine-containing substituents (for example, SO_2CF_3), effective sensitisers have been discovered and these have found applications in the cine-photo industry[61].

Table 3 presents the absorption maxima of carbocyanines, merocyanines, and styryl dyes containing pyridine, 4-methylthiazole, quinoline, and 3,3-dimethylindolenine rings. Apart from carbocyanines, perfluoroalkyl-substituted di- and tricarbocyanines and derivatives of pyridine[62], quinoline[64], and indolenine[68] have been described.

Table 3 shows that the bathochromic influence of perfluoroalkyl groups on the absorption spectra of symmetrical carbocyanines is particularly pronounced in dyes where these substituents have been introduced directly into the heterocyclic nucleus. The substituents in condensed benzene rings usually also exhibit a bathochromic effect but it is weaker and in the case of indolenine derivatives they actually have a hypsochromic effect.

Table 3. The absorption maxima of dyes derived from pyridine (P),[62,63] 4-methylthiazole (T),[63] quinaldine (Q),[64–66] lepidine (L),[64,65,67] and 3,3-dimethylindolenine (I).[68]

Heterocyclic nucleus	Substituent		Carbocyanines		Merocyanines		Styryl dyes	
	in nuclei	at nitrogen atoms	λ, nm	Δλ	λ, nm	Δλ	λ, nm	Δλ
P	2-C_3F_7	CH_3	643	43	584	19	—	—
	2-C_3F_7	C_2H_5	645	42	—	—	547	67
	3-C_3F_7	C_2H_5	610	7	567	17	533	53
	2-$(CF_2)_2$Ph	CH_3					526	
T	5-C_3F_7, 4-CH_3	C_2H_5	563	13	524	−15		
Q	4-CF_3	CH_3	637	32	575	7	571	49
	6-F	C_2H_5	612	7	572	4	536	9
	6-CF_3	C_2H_5	608	3	570	2	558	31
	6-OCF_3	C_2H_5	610	5	—	—	548	21
	6-SCF_3	C_2H_5	617	12	568	0	560	33
	6-SO_2CF_3	C_2H_5	623	18	—	—	586	59
L	2-CF_3	CH_3	731	25	588	28	632	86
	6-F	C_2H_5	718	7	625	11	564	18
	6-CF_3	C_2H_5	717	6	621	7	580	34
	6-OCF_3	C_2H_5	720	9			576	30
	6-SCF_3	C_2H_5	730	19	618	4	586	40
	6-SO_2CF_3	C_2H_5	745	34	618	4	626	80
I	4CF_3	CH_3	540	−8	—	—	—	—
	5-CF_3	CH_3	542	−6	—	—	—	—
	6-CF_3	CH_3	539	−9	—	—	—	—
	5-SCF_3	CH_3	552	+4	—	—	570	25
	5-SO_2CF_3	CH_3	556	+8	—	—	581	36
4,5-Benzo-I	H	$CH_2CF_2CF_2H$	596	+48*	—	—	—	—
	6-CF_3	CH_3	580	−14	—	—	572	14
	6-SCF_3	CH_3	579	−15	—	—	573	15
	6-SO_2CF_3	CH_3	572	−22	—	—	576	18

*Δλ is quoted relative to the dye with the NCH_3 group.

The bathochromic effect of substituents increases when their electron-accepting properties are enhanced. The most electron-accepting group SO_2CF_3 in the 6,6′-positions of the lepidine and quinaldine dyes displaces the absorption bands towards longer wavelengths by 34 and 18 nm respectively.

Comparison of the spectroscopic effects of substituents in dyes with different heterocyclic nuclei (Table 4) shows that these effects are minimal in indolenine derivatives, increase on passing to benzothiazole, benzimidazole, and 2-quinoline derivatives, and are maximum in dyes derived from 4-quinoline.

Table 4. The spectroscopic effects (Δλ) of the fluorine-containing substituents Z in the *p*-position relative to the nitrogen atom.

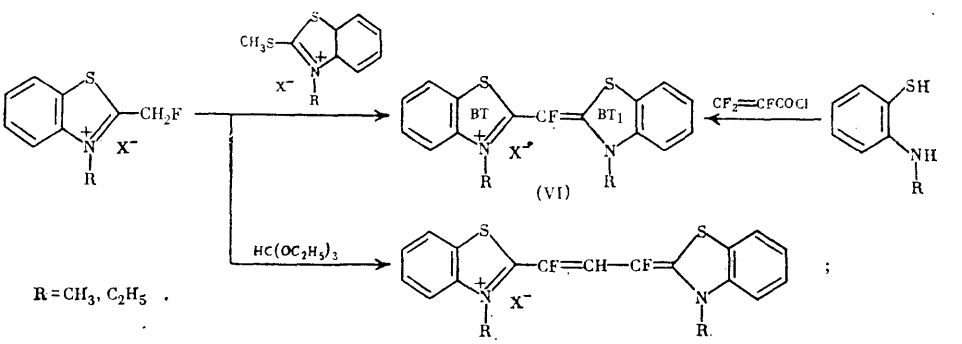
Z	I		BT			BI			Q			L		
	S	C	S	C	M	S	C	M	S	C	M	S	C	M
F	—	—	4	0	—	—	4	1	9	7	4	18	7	11
CF_3	—	−6	18	3	—	—	3	1	31	3	2	34	6	7
OCF_3	—	—	10	2	—	—	4	4	21	5	—	30	9	—
SCF_3	25	4	10	10	—	—	13	6	33	12	0	38	10	4
SO_2CF_3	26	8	36	17	−11	53	18	10	59	18	—	80	34	4

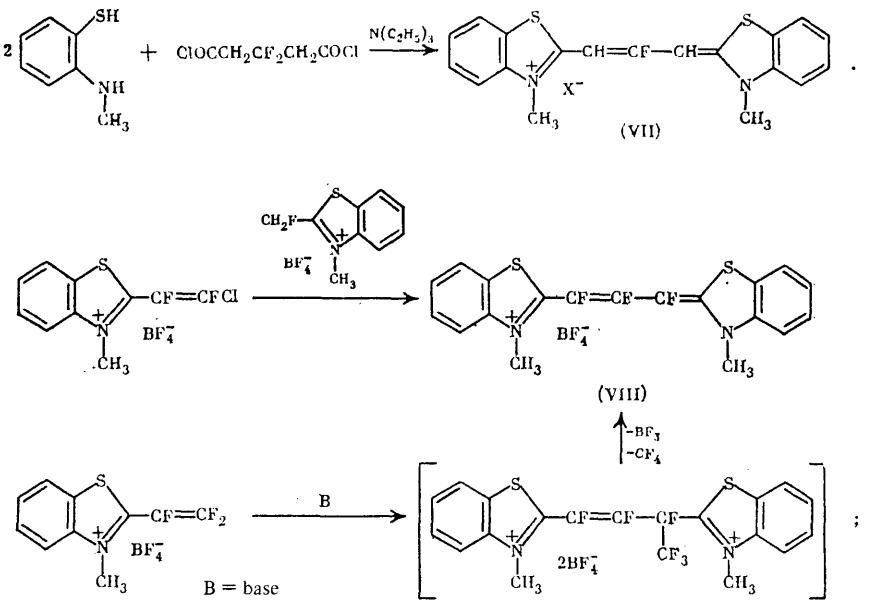
Notation. The following abbreviations for heterocyclic nuclei are used in Tables 4–7 in the names and formulae of the dyes: BT = benzothiazole, BO = benzoxazole, BI = benzimidazole, BS = benzoselenazole, I = indolenine, Q = quinaldine, L = lepidine, R = ethyl- or methyl-rhodanine; the same abbreviations combined with the numeral 1 represent heterocyclic residues in their electron-donating form [see, for example, the formula of dye (VI) in the text]; S = styryl dye; C = carbocyanine; M = merocyanine (derivative of *N*-ethylrhodanine).

Merocyanine dyes, derived from rhodanine, usually exhibit positive solvatochromism, i.e. in polar solvents (alcohols) they have a colour corresponding to a lower frequency than in non-polar (benzene) or less polar (chloroform) solvents[62–67]. However, merocyanines with a benzimidazole nucleus, which exhibit negative solvatochromism, are exceptions[30,31].

2. Dyes with Fluorine-containing Substituents in the Polymethine Chain

The influence of substituents in the polymethine chain on the colour of cyanine dyes has been studied in particular detail in relation to derivatives of benzothiazole. Dyes with a fluorine atom in the α-position in the chain have been synthesised from quaternary 2-fluoromethylbenzothiazolium salts[69] by reactions usually employed to obtain cyanine dyes[69–72]. The dye (VI) can also be synthesised by the reaction of trifluoroacryloyl chloride with *N*-ethyl-*o*-aminothiophenol[73]:





β-Fluorothiacarbocyanine (VII) has been synthesised by the condensation of the dichloride of β,β-difluoroglutaric acid with *N*-methyl-o-aminothiophenol: [74]

The synthesis of α,β-difluoro-substituted dyes has been achieved with the aid of 2-trifluorovinyl or (better) β-chloro-difluorovinyl-benzothiazole and the corresponding quaternary salts [75,76,79]. A dye with a fully fluorinated polymethine chain, namely α,β,γ-trifluorothiacarbocyanine (VIII), has been obtained from the same compounds [76,77,79]:

Other dyes containing fluorine atoms in the polymethine chain have been obtained by analogous procedures (Table 5).

The fluorine atoms in the polymethine chain influence the absorption spectra of the dyes to a much greater extent than those in the heterocyclic nuclei. The influence of the fluorine atom on the spectrum depends on its position in the chain: the introduction of fluorine atoms in the α- and α,γ-positions shifts the absorption band towards longer wavelengths, while the introduction of a fluorine atom in the β-position causes a hypsochromic shift. In conformity with the FKD rule, the electron-donating substituent exerts such an influence [84,85]. Consequently a fluorine atom in the polymethane chain behaves as an electron-donating substituent, which can be explained by the fact that the conjugation of the substituents in the chain exerts a stronger influence on the absorption spectra of the dyes than the inductive effect [84–86].

The introduction of a fluorine atom in the α-position in the heterocyclic residue enhances its electron-donating properties, which entails an increase of the deviation [from coplanarity?] in styryl dyes and a decrease of Δλ (compared with the effect in the symmetrical carbocyanine), while in merocyanine dyes the deviation diminishes and the bathochromic effect of the fluorine atom increases.

The thiacarbocyanine with a fully fluorinated polymethine chain absorbs light at longer wavelengths than the unsubstituted dye and its absorption intensity is higher, which indicates the possibility, in principle, of the existence of a new type of polymethine dyes with fully fluorinated chains.

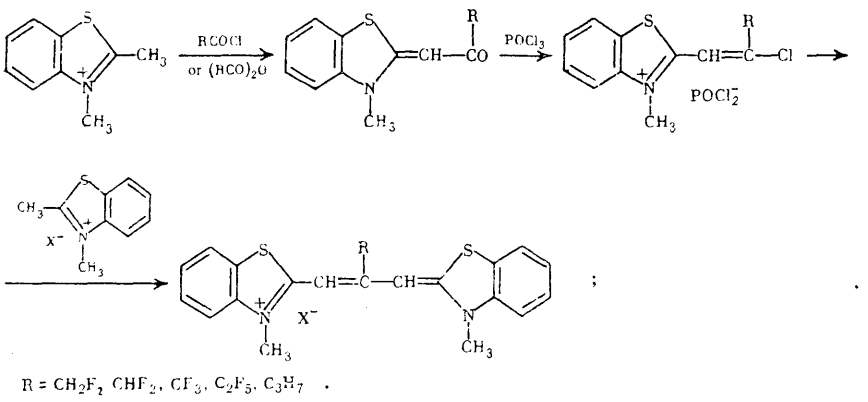
Fluoroalkyl substituents have been introduced only in the β-position of the polymethine chains of cyanine dyes.

Table 5. The absorption maxima of cyanine dyes containing fluorine atoms in the chain.

Formula of dye	λ, nm	Δλ
BT–CF=BT$_1$	453 [69, 73]	30
BT*–CF=CH–CH=BT$_1$	567 [72]	9
BT–CF=CH–CH=BT$_1$	575 [71, 78]	17
BT*–CH=CF–CH=BT$_1^F$	522 [74]	—36
BT*–CF=CH–CF=BT$_1^F$	592 [70]	34
BT–CF=CH–CF=BT$_1$	605 [69]	47
BT*–CF=CF–CH=BT$_1^F$	545 [72, 79]	—13
BT–CF=CF–CH=BT$_1$	547 [71]	—11
BT*–CF=CF–CF=BT$_1^F$	578 [76, 79]	20
BT–CF=CH–CH=CH–CF=BT$_1$	703 [69]	53
BT–CH=CH–CF=CH–CH=BT$_1$	666 [80]	16
BT*–CF=CH–C$_6$H$_4$N(CH$_3$)2-*p*	525 [70]	—3
BT–CF=CH–C$_6$H$_4$N(CH$_3$)2-*p*	532 [69]	2
BT–CF=CF–C$_6$H$_4$N(C$_2$H$_5$)2-*p*	530 [71]	0
BT$_1^F$=CF–CH=R	547 [70]	23
BT*–CF=CH–CH=CH–C$_6$H$_4$N(CH$_3$)2-*p*	570 [81]	—2
BO*–CF=CH–CH=BO$_1^F$	500 [82]	18
BO*–CF=CH–CF=BO$_1^F$	517 [82]	35
BO–CF=CH=CF=BO$_1$	518 [82]	35
BO–CF=CH–C$_6$H$_4$N(CH$_3$)2-*p*	492 [82]	—4
BO$_1$=CF–CH=R	513 [82]	21
Q*–CF=CH–CH=Q$_1$	640	35
Q–CH=CH–CF=CH–CH=Q$_1$	717 [80, 83]	7
H–CH=CH–CF=CH–CH=I$_1$	654 [80, 83]	18
BS–CH=CH–CF=CH–CH=BS$_1$	675 [80]	15

*Methyl groups are attached to the nitrogen atoms of the heterocycles; in the remaining cases the nitrogen atoms are combined with ethyl groups.

The thiacarbocyanine and selenacarbocyanine with the CH_2F group in the β-position have been obtained by the condensation of the corresponding quaternary salts with the iminoester of monofluoroacetic acid [71]. Acylmethylene derivatives and the β-chloroalkenyl-substituted quaternary salts of nitrogen-containing heterocycles have been used to synthesise dyes with other fluoroalkyl groups in the β-position, for example [74]:



$R = CH_2F$, CHF_2, CF_3, C_2F_5, C_3H_7 .

Dyes containing simultaneously fluorine atoms and trifluoromethyl groups in the chain have been synthesised analogously[87] (Table 6).

Table 6. The absorption maxima of cyanine dyes with fluoroalkyl groups in the polymethine chain.

Formula of dye	λ, nm (ethanol)	Δλ
BT* – CH = C(CH_3) – CH = BT†	540 [88]	–18
BT* – CH = C(CH_2F) – CH = BT†	548 [69]	–10
BT* – CH = C(CHF_2) – CH = BT†	568 [74]	10
BT* – CH = C(CF_3) – CH = BT†	581 [74]	23
BT* – CH = C(C_2F_5) – CH = BT†	590 [74]	32
BT* – CH = C(C_3F_7) – CH = BT†	593 [74]	35
BO* – CH = C(CF_3) – CH = BO†	525 [82]	43
Q – CH = C(CH_3) – CH = Q_1	649 [89]	43
BT_1 = CH – C(CH_3) = R	532 [90]	11
BT_1 = CH – C(CH_2F) = R*	538 [74]	17
BT_1 = CH – C(CHF_2) = R*	549 [74]	28
BT_1 = CH – C(CF_3) = R*	555 [74]	34
BT_1 = CH – C(CF_3) = R*	486 [74]	–25
BT* – CF = C(CF_3) – CH = BT†	627 [87]	69
BO* – CF = C(CF_3) – CH = BO†	556 [82]	74
BT* – C(OCH_3) = C(CF_3) – CH = BT_1	624 [87]	66
BT_1 = CF – C(CF_3) = R*	597 [87]	76
BT* – CF = C(CF_3) – C(OH) = BT†	672 ** [91]	114
BT* – C(OCH_3) = C(CF_3) – C(OH) = BT_1	644 ** [91]	86
BT* – CF = C(CN) – CH = BT†	630 ** [92]	74
BT* – C(CN) = CF – CH = BT†	495 ** [92]	–61
BT* – C(CF_3) = CH – $C_6H_4N(CH_3)_2$-p	495 [93]	–53
BT – CH = C(CF_3) – $C_6H_4N(CH_3)_2$-p	530 [93]	2

*See the footnote to Table 5.
**In nitromethane; dyes with the cyano-group are quoted for comparison.

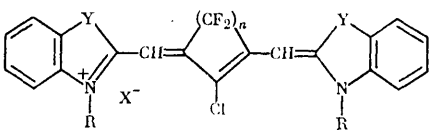
Electron-accepting substituents in the β-position of the polymethine chain of cyanine dyes should exert a bathochromic influence according to the FKD rule. Indeed, the electron-accepting trifluoromethyl groups cause a bathochromic shift of the absorption bands.

Table 6 shows that successive substitution of the hydrogen atoms in the methyl group by fluorine atoms entails a gradual bathochromic shift of the absorption maxima of thiacarbocyanines and merocyanines. In the series of thiacarbocyanines the CH_3 and CH_2F substitutents exhibit hypsochromic effects, while CHF_2, CF_3, C_2F_5, and C_3F_7 exhibit gradually increasing bathochromic effects. A correlation between the absorption frequency and the σ_i and σ_c constants of the substituents has been found for thiacarbocyanines containing substitutents in the β-position[84].

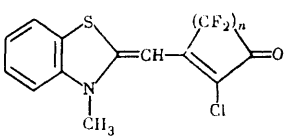
The fluoroalkyl groups in merocyanine dyes derived from benzothiazole exhibit a bathochromic effect, which reflects their electronic and steric influences. The steric hindrance generated by these substituents causes rotation of the predominantly double bond, which entails a bathochromic shift of the absorption bands[74]. In the analogous benzimidazole dye, in which a delocalised ionic structure predominates, the steric hindrance caused by the trifluoromethyl group is responsible for rotation about the predominantly single bond and therefore gives rise to a hypsochromic effect[74].

A spectroscopic effect of the interaction of the substituents is characteristic of cyanine dyes containing electron-donating substituents (fluorine atoms and methoxy-groups) in the α-position of the chain and electron-accepting substituents (trifluoromethyl or cyano-groups) in the β-position: the shift of the absorption band under the influence of two substituents of opposed electronic types exceeds the sum of the shifts induced by the individual substituents in the corresponding monosubstituted dyes[87,91,92]. The bathochromic influence of two electron-donating substituents (F, OH and OCH_3, OH) in the α,γ-positions and of one trifluoromethyl group in the β-position is particularly pronounced (in excess of 100 nm) (Table 6).

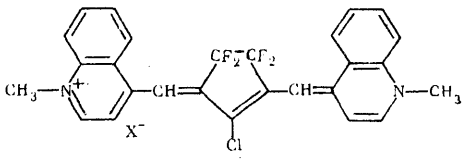
Cyanine dyes containing fluorinated rings in the polymethine chain have been described recently[94,95]:



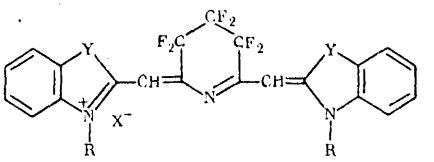
R	Y	n	λ, nm	$\Delta\lambda^*$
CH_3	S	2	660	10
C_2H_5	CH=CH	2	700	-10
C_2H_5	CH=CH	3	758	48



n	λ, nm
2	471
3	500



λ = 773 nm, $\Delta\lambda^*$ = -40 nm



R	Y	λ, nm	$\Delta\lambda^*$
CH_3	CMe_2	572	
CH_3	S	573	9
C_2H_5	CH=CH	621	25

*relative to the dye unsubstituted in the chain.

The fluorinated bridges in the polymethine chains of these dyes can be regarded as electron-accepting perfluoroalkyl substituents, which usually exert a bathochromic influence in conformity with the FKD rule. A hypsochromic influence is observed only in the case of sterically hindered quinoline dyes.

3. Aromatic Azomethines and Azacyanines

The influence of fluorine atoms, trifluoromethyl groups, and other fluorine-containing substituents in the chains of azomethines and azacyanines has been investigated (Table 7). The azomethines (IX) and (X) have been synthesised in accordance with the scheme[96]

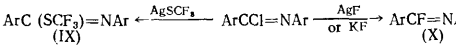
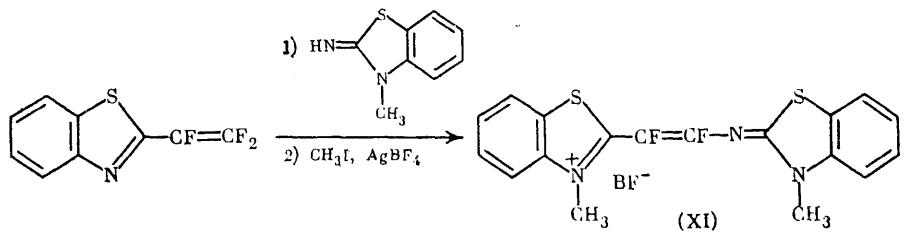


Table 7. The absorption maxima of azomethines and azacyanines with fluorine-containing substituents in the chain.

Formula	λ_{max}, nm (hexane)	Δλ
p-$(CH_3)_2NC_6H_4$-CH = CH-$C_6H_4SO_2CHF_2$-*p*	400 [100]	60
p-$(CH_3)_2NC_6H_4CH = NC_6H_4SO_2CHF_2$-*p*	385 [100]	30
p-$F_2CHSO_2C_6H_4CH = NC_6H_4N(CH_3)_2$-*p*	430 [100]	55
p-$F_2CHSO_2C_6H_4CH = NC_6H_5$	332 [100]	20
p-$(CH_3)_2NC_6H_4CH = NC_6H_4SO_2CF_3$-*p*	395 [100]	40
p-$(CH_3)_2NC_6H_4CH = CH-CH = NC_6H_4SO_2CHF_2$-*p*	410 [100]	
$C_6H_5CF = NC_6H_5$	285 [96, 101]	—27
$C_6H_5C(CF_3) = NC_6H_5$	322 [96, 101]	10
$C_6H_5C(SCF_3) = NC_6H_5$	323 [96, 101]	11
p-$O_2NC_6H_4C(CF_3) = NC_6H_4N(CH_3)_2$-*p*	412 [102]	—38
p-$(CH_3)_2NC_6H_4C(CF_3) = NC_6H_4NO_2$-*p*	365 [102]	—40
p-$O_2NC_6H_4CF = NC_6H_4OCH$-*p*	361 [102]	—14
p-$CH_3OC_6H_4CF = NC_6H_4NO_2$-*p*	310 [102]	—37
BT-CH = CF-N = BT_1	451 * [98]	—16
BT-CF = CF-N = BT_1	477 * [97, 99]	10
BT-CF = C(CN)-N = BT_1	514 * [98]	47
BT-CH = (CF_3)-N = BT_1	453 [99]	—14
BT-CH = $C(C_2F_5)$-N = BT_1	439 [99]	—28
BT-CH = $C(C_3F_7)$-N = BT_1	437 [99]	—30
BT-CF = $C(CF_3)$-N = BT_1	460 [99]	—7

*In nitromethane.



Y = F, Cl ;

$R = CF_3, C_2F_5, C_3F_7$.

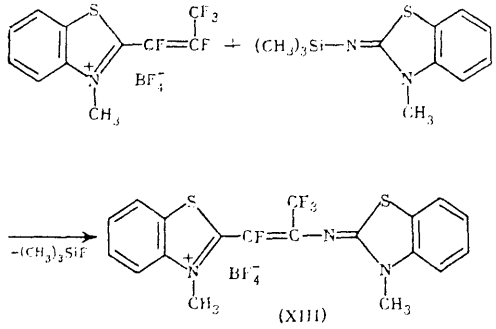
Azomethines with a CF_3 group have been synthesised by the Wittig–Staudinger reaction[96]:

$$ArCOCF_3 + (C_6H_5)_3P{=}NAr \rightarrow ArC(CF_3){=}NAr \ .$$

The azacyanine (XI) with two fluorine atoms in the chain has been obtained from 2-trifluorovinylbenzothiazole[97]: see page 998.

The dyes (XII) with perfluoroalkyl groups in the chain have been synthesised with the aid of the corresponding quaternary benzothiazolium salts[98,99]: see page 998.

The dye (XIII) has been obtained in accordance with the scheme[99]



More complex azomethines with fluorine atoms and trifluoromethine groups in the aromatic nuclei[103] as well as triazacyanines with CF_3 groups in the heterocyclic nuclei[104] have been described. Certain azomethine dyes with CF_3 groups in the nuclei are used in the dyeing of polyester fibres[105,106]. The SO_2CHF_2 and SO_2CF_3 groups in aromatic nuclei have a marked bathochromic effect on the colour of azomethines. The introduction of a fluorine atom in the azomethine groups entails a hypsochromic shift of the absorption bands. The absorption intensity then increases, since the non-planar azomethine molecule usually approaches coplanarity more closely under these conditions[101]. This is probably caused by the fact that the fluorine atom is involved in conjugation with the azomethine linkage. The introduction of a CF_3 group at the methine carbon atom results in a bathochromic effect and reduces the light absorption intensity, since this group gives rise to steric hindrance and enhances the non-coplanarity of the molecule[102].

The sequence in which the ability of the groups to transmit conjugation (to effect the displacement of electrons from left to right) diminishes has been established by comparing the absorption maxima of azomethines containing various substituents in the chain[102]:

$$N{=}CH > N{=}C(CF_3) > CH{=}N > C(CF_3){=}N \text{ and } N{=}CF > N{=}CH > CH{=}N > CF{=}N \ .$$

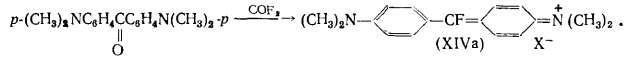
The fluorine atoms in the chains of azacyanines influence the colour like electron-donating substituents, in conformity with the FKD rule, but their spectroscopic effects are weaker than in thiacarbocyanines[97–99]. The influence of perfluoroalkyl groups in the β-position in azathiacyanines depends mainly on the steric hindrance generated by them, which induces rotation of the predominantly single C–N bonds and hence a hypsochromic shift of the absorption bands[99].

III. DIPHENYLMETHANE AND TRIPHENYLMETHANE DYES

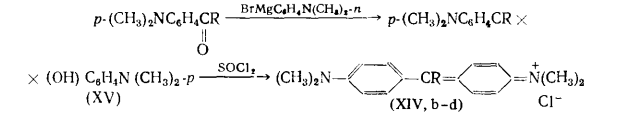
1. Diphenylmethane Dyes

Diphenylmethane dyes containing a fluorine atom or fluoroalkyl groups at the methine carbon atom (compounds XIV, a–d) have been synthesised[86].

A dye with a fluorine atom has been obtained by treating Michler's ketone with difluorophosgene:



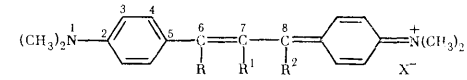
The dyes (XIV, b–d) with R = CHF_2, CF_3, and C_3F_7 have been obtained from the corresponding carbinols (XV):



R	H	F	Cl	CH_2F	CF_3	C_3F_7	CN
λ_{max}, nm	607	588	626	665	693	703	716
$\Delta\lambda$, nm	0	−19	19	58	86	96	109

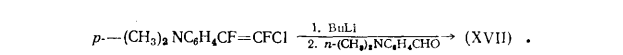
In accordance with the FKD rule, electron-donating substituents have a hypsochromic effect on the colour compared with the unsubstituted dye, while electron-accepting groups have a bathochromic effect. A fluorine atom at the methine carbon atom influences the absorption spectra like an electron-donating substituent, analogously to its influence in the chains of polymethine dyes. Like the cyano-group, fluoroalkyl groups give rise to a strong bathochromic shift of the absorption maximum. A correlation equation relating the absorption frequencies of the dyes to the electronic nature of the substituents (their σ_i and σ_c constants) has been found[86]. The conjugation effects of the substituents R have a preferential influence on the colour. Bulky substituents, for example the CF_3 group, lead to the breakdown of the coplanarity of the dye molecule, reducing the absorption intensity.

The bis(*p*-dimethylaminophenyl)trimethine dye with one or two fluorine atoms in the chain has been synthesised[107]:



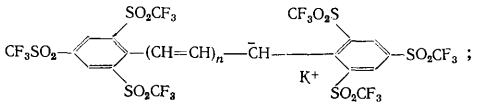
	R	R^1	R^2	$\lambda(CH_3NO_2)$, nm	$\Delta\lambda$
	H	H	H	700	—
(XVI)	F	H	H	693	−7
(XVII)	F	F	H	746	+26

The dye (XVII) has been synthesised in accordance with the scheme



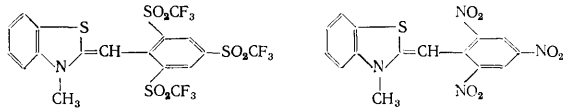
A fluorine atom in the chains of vinylene homologues of diphenylmethane dyes influences the colour like an electron-donating substituent, in conformity with the FKD rule: its effect on the colour is hypsochromic in the even positions within the chain and bathochromic in the odd positions. Both diphenylmethane and polymethine dyes of a new type with a

conjugated anion have been synthesised[108]:



λ_{max}=590 (n=0), 640 (n=1) nm (ethanol).

The analogous anionic dye with nitro-groups absorbs at longer wavelengths (at 622 nm for n = 0), since the SO_2CF_3 group, which is difficult to polarise, is a weaker auxochrome than the nitro-group[108]. This is also evident in relation to the following dyes[109]:

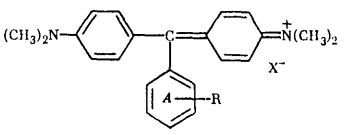


λ_{max} = 504 nm (benzene) λ_{max} = 522 nm (benzene)

2. Triphenylmethane Dyes

Triphenylmethane dyes (analogues of Malachite Green) containing a fluorine atom or a CF_3 group, have been obtained by the Grignard reaction[110,111]. The introduction of the CF_3 group increase the light stability[111]. Crystal Violet with a trifluoromethyl group in the m-position in one of the rings has been synthesised analogously[110].

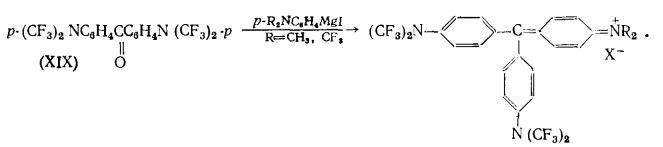
Derivatives of Malachite Green containing one or two trifluoromethylgroups in the A ring [compound (XVIII)] absorb at a lower frequency, like the dyes with an NO_2 group, than the unsubstituted dye[111–113]:



(XVIII)

R	4-CH_3	H	3-CF_3	4-CF_3	4-NO_2	3,5-$(CF_3)_2$	F_5
λ_{max}, nm	616	621	634	637	645	647	658
$\Delta\lambda$	—5	0	13	16	24	26	37

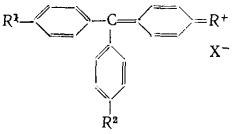
Triphenylmethane dyes containing two trifluoromethyl groups at the nitrogen atom have been synthesised[115]. The analogue of Crystal Violet with one $N(CF_3)_2$ group has been obtained from p-chloro-N,N-bis(trifluoromethyl)aniline and Michler's ketone by treatment with metallic sodium. A fluorine-containing analogue of Michler's ketone (XIX) has been used to obtain dyes with two and three $N(CF_3)_2$ groups:



(XIX)

The replacement of one $N(CH_3)_2$ group in the Crystal Violet by $N(CF_3)_2$ leads to a bathochromic shift of the long-wavelength absorption band by 42 nm. Further substitution of the $N(CH_3)_2$ groups by $N(CF_3)_2$ increases significantly the absorption frequency of the dyes, since the bis(trifluoromethyl)amino-group is a very weak auxochrome[115]. Triphenylmethane dyes containing 2,2,2-trifluoroethyl groups at the nitrogen atom in one or two rings have been proposed for the dyeing of polyacrylonitrile fibre[116].

Triphenylmethane dyes containing one and three $C_2H_5NCH_2.(CF_2CF_2)_nH$ groups, where n = 1, 2, have been synthesised[117]. The absorption maxima of such dyes with n = 1 and 2 hardly differ. The accumulation of the $C_2H_5NCH_2(CF_2CF_2)_nH$ groups in the dye causes a hypsochromic shift of the absorption maximum, although dyes with one such group absorb at a lower frequency, as in the case of $N(CF_3)_2$, than Crystal Violet. The $C_2H_5NCH_2(CF_2CF_2)_nH$ groups are fairly powerful auxochromes, which has been demonstrated also in relation to styryl dyes[117]:

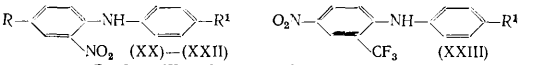


R	R^1	R^2	λ_{max}, nm
$(CH_3)_2N$	$(CH_3)_2N$	$C_2H_5NCH_2CF_2CF_2H$	540, 594
$(CH_3)_2N$	$C_2H_5NCH_2CF_2CF_2H$	$C_2H_5NCH_2CF_2CF_2H$	540, 580
$C_2H_5NCH_2CF_2CF_2H$	$C_2H_5NCH_2CF_2CF_2H$	$C_2H_5NCH_2CF_2CF_2H$	578

IV. NITRODIPHENYLAMINE DYES

Nitrodiphenylamine dyes containing fluorinated groups have found applications as yellow disperse dyes for artificial and synthetic fibres. Dyes of this type have been obtained by the condensation of substituted chlorobenzenes containing the CF_3,[118–120] CF_3CO,[121] or CF_3SO_2 [119,122] groups with arylamines.

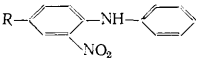
The dyes (XX)–(XXII) produce yellow coloure on acetate silk and Lavsan with a high stability in relation to light soap, and sublimation[121,124,125]:



(XX)–(XXII) (XXIII)

R=CF_3 (XX), SO_2CF_3 (XXI), $COCF_3$ (XXII);
R^1=H, CH_3O, C_2H_5O, Cl, CH_3, $NHCOCH_3$.

The fastness to light of trifluoroacetophenone (XXII) derivatives reaches 7 units, which is lower by 1–2 units than for the corresponding acetophenone derivatives; the stabilities in relation to soap, friction, and sublimation are different. The nitrodiphenylamine dye (XX, R = H) has a higher light stability than its isomer with the NO_2 group in the p-position[126]. The introduction of a second nitro-group into the dye (XX, R = H) in the 6-position lowers the fastness to light[127]. Electron-donating substituents R in 2-R-4-NO_2- and 4-R-2-NO_2-diphenylamines produce a bathochromic shift of the long-wavelength band, while electron-accepting substituents give rise to a hypsochromic shift of the absorption maximum[120,128,129]. Such influence of the substituents is consistent with the FKD rule:



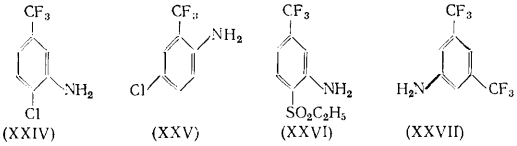
R	CH_3O	H	CF_3CO	CF_3	CF_3SO_2	NO_2
λ_{max}, nm (alcohol)	465	425	417 (benzene)	410	397	353
$\Delta\lambda$	40	0	—8	—15	—28	—72

The substituents R^1 in the dyes (XX) and (XXIII) have an analogous influence, but it is weaker than that of the substituent R.

Nitrodiphenylamine dyes exhibit positive solvatochromism, for example, for the dye (XX, R = H), λ_{max} is 432 nm in water, 410 nm in alcohol, and 401 nm in hexane.

V. AZO-DYES

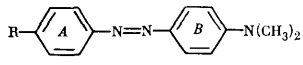
Azo-dyes with fluorine-containing substituents constitute a large group of disperse, cold, cationic, and active dyes. They are used to dye natural, artificial, and synthetic fibres and frequently exhibit a high stability in relation to light, oxidation, and other physical and chemical influences. Fluorine-containing substituents have been introduced into both diazo- and azo-components. The methods for their introduction have been satisfactorily developed[6,7,132]. The azoamines (XXIV)–(XXVII) with a trifluoromethyl group are used for the cold dyeing of cotton[130,131]. They are manufactured on an industrial scale.



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

These amines give rise to brilliant fast orange and red colours. The dyes based on the azoamines Brilliant Orange K (XXIV) and Brilliant Yellow G (XXV) are particularly brilliant and light-fast.

Table 8. The absorption maxima of dimethylaminoazo-dyes and their salts[133–137]

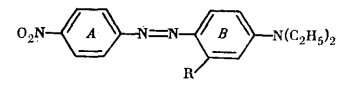


R	λ_{max}, nm		$\Delta\lambda$*	R	λ_{max}, nm		$\Delta\lambda$
	alcohol	alcohol + HCl			alcohol	alcohol + HCl	
CH_3O	497	555	148	CF_3	427	505	78
CH_3S	420	555	135	$(CF_3)_3CS$	444	512	68
CH_3	467	533	126	CHF_2SO	445	511	66
H	407	518	111	CF_3SeO	448	510	62
F	407	518	111	CF_3SO	447	507	60
Cl	417	522	105	$(CF_3SO_2)_2N$	449	507	58
CF_3O	419	512	93	CHF_2SO_2	463	503	40
CHF_2S	429	520	91	FSO_2	463	498	35
CF_3Se	430	517	87	NO_2	475	508	33
CF_3S	432	514	82	CF_3SO_2	476	500	24
CF_3SO_2O	424	508	84	$(CF_3)_3CSO_2$	485	500	15

*$\Delta\lambda = \lambda_{max}$(alcohol + HCl) − λ_{max}(alcohol).

Table 8 lists the absorption maxima of dimethylaminoazobenzenes (DAAB), containing fluorinated groups in the diazo-component of the dye. The absorption maxima of DAAB with electron-donating substituents give rise to a bathochromic shift of the absorption maximum, which is greater the more pronounced the electron-accepting properties. A fluorine atom does not influence the absorption spectrum. The CHF_2SO_2 and FSO_2 groups have effects similar to that of the NO_2 group, while the CF_3SO_2 and $(CF_3)_3CSO_2$ groups have a more marked influence and are the most powerful electron acceptors. When the molecules of azo-dyes are excited by light, electrons are displaced from the *B* ring to the azo-group and the *A* ring. Electron-accepting groups in the *A* ring and electron-donating groups in the *B* ring therefore as a rule cause a bathochromic shift in the colour of azo-dyes. The excitation of the molecules of salts of azo-dyes is accompanied by an electron shift in the opposite direction.

The absorption maxima of azo-dyes in an acid medium undergo a bathochromic shift after the introduction of electron-donating substituents into the *A* ring and electron-accepting substituents into the *B* ring (Table 8).[133,138,139] The influence of substituents in the *B* ring is illustrated below:



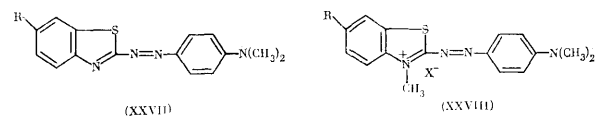
	R	CH_3O	CH_3	H	F	NO_2	CF_3	CN
λ_{max}, nm	alcohol	501	497	486	469	470	467	472
	alcohol + HCl	486	513	515	505	514	530	550
	$\Delta\lambda$	−15	16	29	36	44	63	78

(The difference between the absorption maxima of the DAAB derivatives and their salts is an indication of the halochroism of azo-dyes. It is linearly related to the Hammett σ constants of the substitutents:

$$\Delta\lambda = 125-101\sigma_p \ (r = 0.997); \quad \Delta\lambda = 115-70\sigma_m \ (r = 0.986).$$

Analogous equations have been obtained for *N*,*N*-di-(hydroxyethyl)aminoazo-dyes[133] and the bases of diazastyryl dyes (XXVII).[140]

The influence of substituents in the 6-position of the benzothiazole ring on the colour of the bases (XXVII) and the diazastyryl dyes (XXVIII)[140] is analogous to their influence in DAAB and their salts:

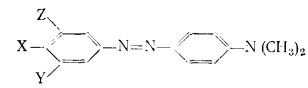


(XXVII) (XXVIII)

	R	CH_3O	CH_3	H	CF_3O	CF_3	CF_3S	CF_3SO	NO_2	CF_3SO_2
λ_{max}, nm	alcohol	511	510	509	518	526	529	536	548	546
	alcohol + HCl	610	600	508	596	598	588	584	584	562
	$\Delta\lambda$	99	90	89	78	62	59	51	36	16

The curves and the absorption maxima for the diazastyryl derivatives (XXVIII) and the hydrochlorides of the bases (XXVII) do not differ. This shows that the proton adds to the nitrogen atom in the benzothiazole ring and not the azo-group. Despite the difference between the structures of the diazastyryl dyes and DAAB, the influence of their substituents is of the same type.

The introduction of electron-donating substituents into DAAB leads to high values of $\Delta\lambda$ (Table 8). These dyes possess indicator properties. Lower values of $\Delta\lambda$ correspond to electron-accepting substituents. Such dyes are less halochromic and more suitable for the dyeing of fabrics and they are resistant to the gases in smoke. The introduction of highly electron-accepting fluorine-containing groups into the DAAB molecule makes it possible to observe the influence of negative halochroism—a hypsochromic shift of the absorption maximum in an acid medium[138]:



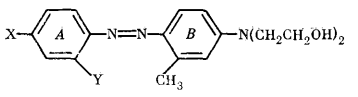
X	Y	Z	λ_{max}, nm		$\Delta\lambda$
			alcohol	alcohol + HCl	
NO_2	CF_3	—	487	503	16
CF_3	CF_3	CF_3	493	493	0
CH_3SO_2	CF_3SO_2	—	497	494	−3
CF_3SO_2	NO_2	—	522	490	−32

The negative halochroism can be explained by the fact that, in the case of strong electron-accepting substituents, the boundary resonance structures of the dye base approach energetic equivalence. Such dyes absorb at low frequencies.

After the introduction of electron-accepting substituents into the dye salts, there is a sharp increase of the contribution of the structure (which is dominant in any case) having a positive charge on the nitrogen atom of the dialkylamino-group, which causes a hypsochromic shift in the colour of the dye compared with the colour in a neutral medium.

A valuable quality of many fluorine-containing azo-dyes is high fastness to light in which the position and character of the fluorinated groups play a major role (Table 9).[141] When the electron-accepting properties of the substituents in the *o*- and *p*-positions in monosubstituted dyes (Nos.1–13) are enhanced, a bathochromic shift is observed. *p*-Substituted dyes (Nos.10 and 12) absorb at longer wavelengths than the *o*-isomers (Nos.11 and 13). Monosubstituted dyes with electron-donating and weak electron-accepting substituents (Nos 1, 2, and 4–9) are less light-fast than the unsubstituted dye (No.3). Electron acceptors (the nitro- and trifluoroethanesulphonyl groups) increase somewhat the light-fastness. No differences are observed between the light-fastnesses of monosubstituted dyes with the same substituent in the *o*- and *p*-positions.

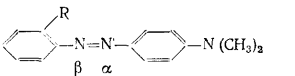
Table 9. The absorption maxima and fastness to light of fluorine-containing azo-dyes[141]



(XXIX)

No.	X	Y	λ_{max}, nm		Fastness to light, units
			alcohol	alcohol + HCl	
1	CH_3	H	416	538	3
2	H	CH_3	418	522	3
3	H	H	415	524	5
4	CF_3O	H	424	515	3–4
5	H	CF_3O	430	505	3–4
6	CF_3	H	434	509	3
7	H	CF_3	434	492	3–4
8	CF_3S	H	440	515	2–3
9	H	CF_3S	438	508	3
10	NO_2	H	492	520	5–6
11	H	NO_2	450	518	5
12	CF_3SO_2	H	484	503	5–6
13	H	CF_3SO_2	470	493	5–6
14	CF_3	NO_2	485	504	4–5
15	NO_2	CF_3	522	490	6–7
16	CF_3S	NO_2	490	510	4–5
17	NO_2	NO_2	533	504	5
18	CF_3SO_2	NO_2	538	492	5
19	NO_2	CF_3SO_2	564	484	6–7

Among the isomeric disubstituted dyes Nos.14 and 15 and Nos.18 and 19, the dyes Nos.15 and 19 containing the CF_3 and CF_3SO_2 groups in the *o*-position, absorb at the lowest frequencies and show the greatest fastness to light. For the substituent in the *p*-position, the length of the chromophore chain has the greatest influence on the colour. The trifluoromethanesulphonyl group, which is a stronger electron acceptor than the nitro-group like all sulphur-containing substituents, has a tetrahedral structure. Conjugation does not therefore reach the oxygen atoms, being restricted to the sulphur atom by virtue of the involvement of its *d* orbitals and the conjugation chain is shorter than for the *p*-NO_2 group[147]. The conjugation of the *o*-NO_2 group is greatly influenced by steric factors. The breakdown of coplanarity for the CF_3SO_2 group does not affect significantly its conjugation with the dye chromophore. The fastness to light of the disubstituted dyes depends on the positions of the substituents. Dyes Nos.15 and 19 are more light-fast than dyes Nos. 16–18. This can be apparently explained by the fact that the bulky electron-accepting CF_3 and CF_3SO_2 groups in the *o*-position relative to the azo-group protect the latter against photochemical oxidation to a greater extent than the nitro-group. This is confirmed by the comparison of the absorption intensities of the salts of substituted DAAB.[145] Even a proton, which is small, adds to only an insignificant extent to the β-nitrogen atom of the azo-group in the presence of the CF_3 group in the *o*-position.



λ_{max}, nm (10^{-4} *E* given in brackets)

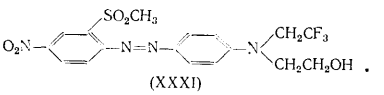
R	alcohol	alcohol + HCl
CH_3	410 (2.70)	520 (1.00)
H	407 (2.80)	518 (4.60)
CF_3	425 (2.98)	479 (0.008)
NO_2	440 (2.68)	500 (1.11)

In order to obtain light-fast dyes, it is necessary that two electron-accepting substituents be present in the *A* ring. A bulky fluorine-containing group in the *o*-position has a favourable effect. In those dyes where a trifluoromethyl group is already present in the *o*-position relative to the azo-group, the introduction of a bromine atom or a CF_3 group in the second *o*-position does not lead to a further increase of the fastness to light of the colour[146].

Among the dyes of type (XXIX) (Table 9), those where X = NO and Y = CF_3, C_2F_5, CF_2SO_2, or CHF_2SO_2 exhibit the highest light-fastness for different azo-components. Such dyes are of practical interest[146–164]. Stable colours on polyamide and polyester fibres have been obtained by dyeing the latter with disperse azo-dyes containing the fluorosulphonyl group[165–167]. The azoamines (XXIV)–(XXVII) [168–180] as well as their trifluoromethanesulphonyl analogues[181,182] are used to prepare pigments of cold, disperse, cationic, and azid azo-dyes. Disperse and cationic azo-dyes based on hereocyclic diazo-components, obtained from amino-derivatives of thiazole, thiadiazole, benzothiazole and pyrazole containing the CF_3 and $(CF_3)_2COH$ groups, are of practical interest for the colouring of artificial and synthetic fibres[183–190]. Certain disperse azo-dyes containing the CF_3 [191–196] and $COCH_3$ [197] groups have a low stability in relation to sublimation. Because of this "deficiency" they have found applications as dyes for thermal transfer printing on polyester and polyamide fibres. Dyes with the CHF_3, SO_2F, SO_2CHF_2, and SO_2CF_3 substituents in the benzoisothiazole ring, used for transfer printing on polyacrylonitrile and polyester fibres, are also mentioned in a patent[194].

The arylamines $C_6H_5NRCH_2CH_2OH$ (XXX),[198] where R = $C_3F_7CH_2$, CF_3CH_2, CHF_2CH_2, $CH_3CF_2CH_2$, $CF_3CH_2CH_2$, $CHF_2CH_2CH_2$, $CH_3CF_2CH_3CH_2$, CH_2FCH_2, $CH_3CF_2CF_2CH_2CH_2$, or $CH_3CF_2CH_2CH_2CH_2$ are used as the azo-component. They have been obtained by the reaction of aniline with fluorine-containing alkyl bromides followed by treatment with epoxyethane[199,200]. The study of the properties of azo-dyes with azo-components of type (XXX) has shown that, with increase of the distance between the nitrogen atom and the carbon atom linked to the fluorine atom and with decrease of the number of fluorine atoms in the alkyl group, the colour of the dyes shifts bathochromically. The fastness to light increases with increase of the number of fluorine atoms in the *N*-alkyl group and as they come closer to the nitrogen atom[201]. The dye (XXXI) on acetate silk[201] and the dyes with the $N(CH_2)_nC_2F_5$ (n = 1, 2) groups in the azo-component on

polyester fibre[202–206] show an excellent fastness to light.



(XXXI)

Many new fluorine-containing azo-components $C_6H_5NRCH_2.(CF_2CF_2)_nH$ (XXXII, R = H, CH_3, C_2H_5, C_2H_4OH, or C_2H_4CN; n = 1, 2) have been synthesised by alkylating arylamines with the polyfluoroalkanesulphonates of fluorinated telomeric alcohols $H(CF_3CF_2)_nCH_2OH$ (FTA).[207,208]

The substituents R in disperse azo-dyes obtained from the azo-components (XXXII) can be arranged in the following sequence in terms of the bathochromic shift of the colour: $C_2H_5 \geq C_2H_4OH > CH_3 > C_2H_4CN$.[209] An increase in the number of difluoromethylene groups n leads to a hypsochromic shift of the absorption maximum by 6–7 nm. All the dyes exhibit a high fastness to light and some of them readily sublime and are suitable for thermal transfer printing.

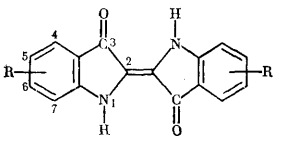
Dyes containing the CF_3 groups in the *o*-positions of the benzene ring of the azo-component are more light-fast than the corresponding dyes with the CH_3 group[140,210,217].

The absorption spectra and fastness to light of disperse azo-dyes derived from *N*-(2,2,2-trifluoroethyl)tetrahydroquinoline have been investigated[216].

The active dyes in which fluorine-containing groups, for example, a fluorine-substituted triazine or polyfluorocyclobutyl group[218–221], form a strong linkage with the fibre, are widely used, although certain fluorine atoms are then substituted and are no longer present in the dye on the fibre. If trifluoromethyl groups are present in the molecules of the azo-dyes forming part of the active dye[222–228], then such dyes give rise to light-fast colours.

VI. INDIGOID AND THIOINDIGOID DYES

Isatins and indigoid dyes containing fluorine atoms and trifluoromethyl groups have been described[126,229–234]. Electron-donating substituents in the 5,5′-positions in indigo cause a bathochromic shift in the colour, while electron-accepting substituents cause a hypsochromic shift. The substituents in the 6,6′-positions act in the opposite manner.

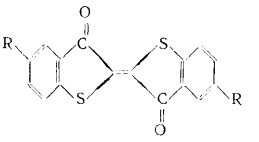


λ_{max}, nm (tetrachloroethane)

R	5,5′	6,6′	4,4′	7,7′
CH_3O	645	570	—	—
H	605	605	605	605
F	615	570	—	560
CF_3	—	—	605	580
NO_2	580	635	—	—

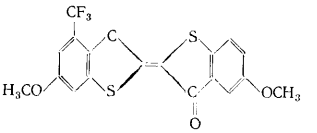
The fluorine atoms in the 5,5′- and 6,6′-positions influence the colour like electron-donating substituents. The inductive effect of the substituents in the 7,7′-positions has a marked influence. Fluorine atoms give rise to a greater hypsochromic shift of the absorption maximum of the dye than the CF_3 group. Comparison of the stabilities of the colours of 5,5′- and 7,7′-difluoroindigos with that of the colour of 5,5′-dibromoindigo showed that the fluoro-derivatives are more light-fast[234].

The replacement of the ethyl group in the vat dye diethoxyviolanthrone by the trifluoroethyl group causes a hypsochromic shift in the colour of the dye—the latter changes from green to blue[126]. Derivatives of thioindigo containing fluorine atoms and fluorinated groups have been obtained by oxidising the corresponding thionaphthenes[235–239]:



R	F	H	CF_3O	CF_3S	CF_3	NO_2
λ_{max}, nm (benzene)	559	545	549	548	535	513
$\Delta\lambda$	14	0	4	3	−10	−32

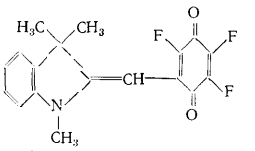
Electron-accepting substituents in the 5,5′-positions of thioindigo hinder the shift of electrons from the sulphur atom to the carbonyl group. This leads to a hypsochromic shift of the absorption maximum of the dye. $\Delta\lambda$ diminishes in the following sequence of substituents in the 5,5′-positions: C_2H_5O > I > F, Cl, Br > CH_3 > CF_3O > CF_3S > H > CF_3 > CH_3SO_2 > NO_2. 5,5′-Bis(trifluoromethyl)thioindigo derivatives exhibit a weak affinity for fibre[239]. Asymmetric dyes of the type



impart a bright red and fast colour to cotton, which makes them suitable for dyeing and printing[236].

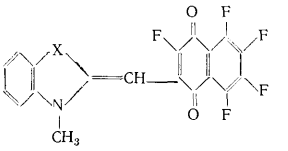
VII. BENZOQUINONE, NAPHTHOQUINONE, AND ANTHRAQUINONE DYES

The merocyanine dyes (XXXII) and (XXXIII) have been obtained by the reaction of methylene-substituted bases of nitrogen-containing heterocycles with the corresponding perfluoroquinones[240]:



(XXXII)

λ_{max}, nm	$\Delta\lambda$
692	+38

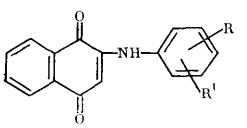


(XXXIII)

X	λ_{max}, nm	$\Delta\lambda$
$C(CH_3)_2$	635	+35
S	668	+53
CH=CH	685	+15

The introduction of fluorine atoms into the quinonoid nuclei of dyes leads to a considerable bathochromic shift. Like the corresponding compounds without fluorine, the dye (XXXII) with a perfluorobenzoquinone ring absorbs at longer wavelengths than the dye (XXXIII) with a perfluoronaphthoquinone residue. As the electron-donating properties of the heterocyclic residues are enhanced, the colour of the dye changes bathochromically.

Napthoquinone dyes (2-phenylamino-1,4-naphthoquinones) containing fluorinated groups in the benzene ring have been synthesised[241].

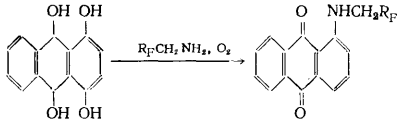


R, R′	λ_{max}, nm	R, R′	λ_{max}, nm
H, H	462	H, 3-CF_3	449
H, 4-F	460	H, 3-NO_2	443
H, 4-CF_3O	456	2-Cl, 5-CF_3	441
H, 4-CF_3S	454	2-NO_2, 5-CF_3	438
H, 4-CF_3SO_2	440	2-Cl, 5-CF_3SO_2	426

Fluorine-containing substituents shift the absorption maximum of the dye towards shorter wavelengths, since they withdraw electrons from the amino-group and prevent their transfer to the oxygen atom. Naphthoquinone dyes with fluorine-containing substituents are faster in relation to all kinds of treatment on Lavsan than dyes of the same series with non-fluorinated groups.

2-Trifluoromethylanthraquinone has been used as an intermediate in the synthesis of vat dyes[242]. 1-Isocyanato-5-trifluoromethylanthraquinone has been recently patented for the same purpose[243].

Dyes of the aminohydroxyanthraquinone series containing fluoroalkyl substituents at the nitrogen atom of the amino-group, have been obtained by treating leucoquinizarin with fluoroalkylamines and subsequent oxidation[244]:

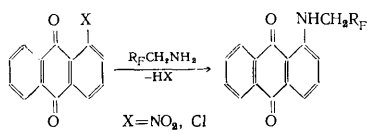


Fluorine-containing alkyl substituents in the alkylamino-group induce a hypsochromic shift and increase the fastness to light of the dyes in the sequence $CH_3CF_2CH_2CH_2CH_2$, $CHF_2CH_2CH_2 < CH_3CF_2CH_2 < CHF_2CH_2$, CF_3CH_2, $CH_3(CF_3)CH$ (Table 10).

Table 10. The absorption maxima of anthraquinone derivatives containing polyfluoroalkyl groups[246].

No.	Ring substituents	λ_{max}, nm	
		methylene chloride	alcohol
1	1-NH_2	465	483
2	1-$NHCH_2CF_2CF_2H$	470	480
3	2-NH_2	410	452
4	2-$NHCH_2CF_2CF_2H$	420	450
5	1,4-$(NH_2)_2$	545, 582	552, 593
6	2-$NHCH_2(CF_2CF_2)_2H$	—	442
7	1,4-$(NHCH_3)_2$	620	593, 641
8	1,4-$(NHCH_2CF_2CF_2H)_2$	555, 594	568, 608
9	1-OH	405	408
10	1-$OCH_2CF_2CF_2H$	336	367
11	1-$OCH_2(CF_2CF_2)_2H$	343	351
12	2-OH	365	380
13	2-$OCH_2CF_2CF_2H$	328	330
14	1-NH_2-4-OH	528, 554	534, 570
15	1-$NHCH_2CF_2CF_2H$-4-OH	534, 570	537, 571
16	1-NH_2-4-Cl	472	484
17	1-NH_2-4-$OCH_2CF_2CF_2H$	476	496
18	1-NH_2-4-$OCH_2(CF_2CF_2)_2H$	476	496

α-Polyfluoroalkylaminoanthraquinone dyes have also been synthesised by the reaction of fluoroalkylamines with α-nitroanthraquinone[245] or α-chloroanthraquinone[246]:



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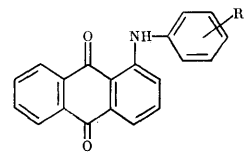
1,4-Bis(1′,1′,3′-trihydrotetrafluoropropyl)anthraquinone has been obtained by substituting two hydroxy-groups in leucoquinizarin by polyfluoroalkylamino-groups. The same product as well as β-polyfluoroalkylaminoanthraquinone has been synthesised by alkylating aminoanthraquinones by FTA sulphones[246,247]. When α- and β-chloroanthraquinones were treated with sodium alkoxides derived from FTA, polyfluoroalkoxyanthraquinones were obtained[246].

The substitution of the hydrogen atom of the hydroxy-group by a polyfluoroalkyl group influences the absorption maximum to a greater extent than the substitution of a hydrogen atom in the amino-group; the colour undergoes a hypsochromic shift to the extent of 50 nm. The β-polyfluoroalkylamino- and β-polyfluoroalkoxy-anthraquinones have colours in a shorter wavelength range than the corresponding α-derivatives.

The substitution of two hydrogen atoms in 1,4-diaminoanthraquinone (one in each amino-group) induces a bathochromic shift of the absorption band of the residue by 15 nm. However, dye No.8 (Table 10) has a colour corresponding to a much shorter wavelength than 1,4-bis(methylamino)-anthraquinone (No.7).

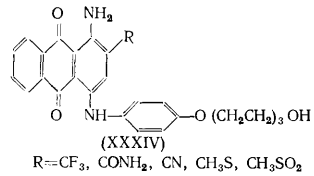
1-Amino-4-polyfluoroalkoxyanthraquinones (Nos.17 and 18) have only one absorption maximum in the visible region, in contrast to 1-amino-4-hydroxy- and 1,4-diamino-anthraquinones, because the polyfluoroalkoxy-groups are not involved in conjugation with the carbonyl group and in the formation of the hydrogen bond.

Arylaminoanthraquinone dyes containing fluorinated substituents in the benzene ring are suitable as disperse dyes for synthetic fibres. Electron-donating substituents in the benzene ring, like those introduced directly into the anthraquinone nucleus, induce a bathochromic shift of the absorption maximum of the dye, while electron-accepting substituents give rise to a hypsochromic shift[249].



R	λ_{max}, nm (alcohol)		
	p-	*m*-	*o*-
CH_3O	515	506	521
H	508	508	508
CF_3	496	492	486
NO_2	482	486	481

Dyes containing the CF_3 group impart to polyester fibre a red colour which is fast to light[248–251]. Comparison of the stabilities of the colours on acetate silk showed that the dye (XXXIV), containing the CF_3 group, has the highest fastness to light[244]:



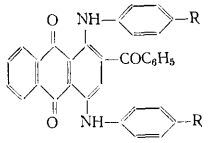
(XXXIV)

R=CF_3, $CONH_2$, CN, CH_3S, CH_3SO_2 .

The CF_3O group has been introduced into arylaminoanthraquinones in addition to the CF_3 group[252,253]. Colours more resistant to wet treatments and light have been obtained on polyester fibre than in the case of fluorine-free dyes. A series of 4-arylamino-1-hydroxyanthraquinones with substituents in the benzene ring [CF_3,[254,255] CHF_2,[256] OCF_2CHFX (X = H, F, or Cl),[257] CF_3O,[253] $C(CF_3)_2OH$ [258]] as well as pentafluorobenzamidoanthraquinone[259] have been patented.

1,4-Diarylaminoanthraquinones are obtained by arylating 1,4-diaminoanthraquinone. The substitution of the *p*-position in the benzene ring by the fluorine-containing groups CF_3CO and CF_3SO_2 leads to a hypsochromic shift of the long-wavelength absorption maximum as a consequence of the electron-accepting influence of such groups: $CF_3SO_2 > NO_2 >$

$CF_3CO > H > CH_3$:[260,261]



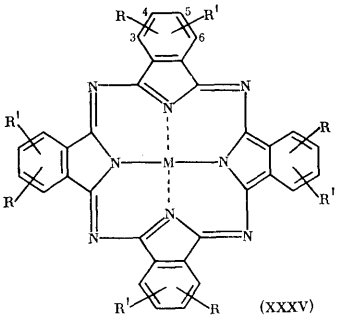
R	λ_{max}, nm (trichlorobenzene) ($\Delta\lambda$)	
CH_3	442 (10)	677 (11)
H	432	666
CF_3CO	440 (8)	617 (—49)
NO_2	448 (16)	612 (—54)
CF_3SO_2	419 (—13)	595 (—71)

These dyes impart to polyester fibre a bright green colour with high parameters of resistance to all physical and chemical influences. Patents describe 1,4- and 1,5-diarylaminoanthraquinone dyes containing the CF_3,[262–264] CF_3O, CF_3CO, CF_3SO_2,[260,261,265,266] $OCHF_2$, and OCF_2CHF_2 [267] groups in the benzene ring. They are used to impart fast blue and green colours to cellulose esters, polyesters, and polyamides.

VIII. PHTHALOCYANINE DYES WITH FLUORINE-CONTAINING SUBSTITUENTS

The introduction of fluorine atoms and fluorine-containing substituents into phthalocyanine dyes not only influences their absorption spectra but also increases their fastness to light, solubility, and resistance to the action of oxidants.

Table 11 lists the absorption maxima of metal-free phthalocyanines[268–270], copper-containing phthalocyanines (XXXV), and naphthalocyanines[270]:



(XXXV)

Table 11. The absorption maxima of fluorine-containing phthalocyanines (Pc) and naphthalocyanines (Nc).[268–270]

No.	Compound	λ_{max}, nm (in C_6H_5Cl)	No.	Compound	λ_{max}, nm (in C_6H_5Cl)
1	PcH_2	92, 665, 638, 601 [271]	14	$(CF_3S)_4$-3-PcH_2	701, 670, 639
2	PcCu	578, 648, 611 [271]	15	$(CF_3S)_4$-3-PcCu	682, 625
3	Γ_4-3-PcCu	680, 646, 611 [271]	16	$(CF_3S)_4$-4-PcH_2	699, 663, 645, 633, 603
4	F_4-4-PcCu	666, 632, 597 [271]	17	$(CF_3S)_4$-4-PcCu	679, 610
5	$(CF_3)_4$-3-PcH_2	681, 646, 620, 584	18	$(CF_3S)_8$-4,5-PcH_2	708, 675, 652, 612
6	$(CF_3)_4$-3-PcCu	660, 631, 595	19	$(CF_3S)_8$-4,5-PcCu	687, 616
7	$(CF_3)_4$-4-PcCu	669, 637, 601	20	$(CF_3SO_2)_4$-4-PcH_2	700, 672, 636, 610
8	$(CF_3)_8$-4,5-PcCu	669, 639, 601	21	$(CF_3SO_2)_4$-4-PcCu	682, 610
9	$(CF_3)_8$-3,6-PcH_2	702, 674	22	NcCu	776, 695
10	$(CF_3)_8$-3,6-PcCu	680, 616	23	$(CF_3)_4$-6-NcCu	770, 688
11	$(CF_3)_{12}$-3,4,5-PcCu	669, 639, 602	24	$[(CF_3)_3C]_4$-6-NcCu	772, 684
12	$[(CF_3)_3C]_4$-4-PcH_2	692, 655, 593	25	$(CF_3)_8$-6,7-NcCu	766, 714, 678
13	$[(CF_3)_3C]_4$-4-PcCu	672, 602			

*PcH_2 = phthalocyanine without a metal; PcCu = copper-phthalocyanine; NcCu = copper-naphthalocyanine.

The fluorine atoms in the 4-position in the phthalocyanines have virtually no influence on the absorption maxima and those in the 3-position induce a small bathochromic shift. A hypsochromic shift of the absorption bands is characteristic of tetrakis(trifluoromethyl)phthalocyanines (dyes Nos.5–7). The introduction of two or three trifluoromethyl groups in the 4- and 5-positions (dye No.8) or 3-, 4-, and 5-positions (dye No.11) does not induce a shift of the absorption maximum compared with the 4-substituted dye (No.7). The perfluoro-t-butyl group (dyes Nos.12 and 13) hardly affects the position of the long-wavelength absorption maximum. The trifluoromethylthio- and trifluoromethanesulphonyl-groups in dyes Nos.14–21 exhibit small bathochromic effects.

A bathochromic shift of the absorption band by approximately 100 nm is observed in the absorption spectra of naphthalocyanines (Nos.23–25) compared with the perfluoroalkylphthalocyanines.

The introduction of trifluoromethyl and perfluoro-t-butyl groups into phthalocyanine molecules greatly increases their solubility in organic solvents, reduces their basicity, and increases their resistance to oxidation[269].

It is seen from the above that investigations have led to the discovery of certain rules governing the influence of fluorine atoms and fluorine-containing substituents on the colour and properties of all classes of organic dyes. These data can be used for the specific synthesis of dyes with practically valuable properties.

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The Phosphorus-Carbon Prototropic Tautomerism

T.A.Mastryukova and M.I.Kabachnik

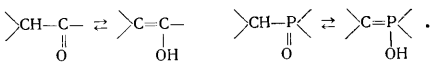
New types of prototropic tautomerism in which the proton migrates between a carbon atom and a phosphorus-containing functional group are examined. It is shown that in all cases the position of the tautomeric equilibrium is determined by the relative acidities of the different forms: the CH acidity of the forms in which the proton is located at a carbon atom and the PH or PXH acidity (X = O, S, etc.) of the tautomers with the proton in the phosphorus-containing group. The method for the estimation of the relative acidities of different forms with the aid of the σ^{ph} constants of the substituents at the phosphorus atom and the σ_C^- constants of the substituents at the central carbon atom, characterising the acidifying influence of these substituents, has attracted attention in this connection.
It has been shown that in all cases the equilibrium position is determined by the general characteristics of the protolytic acid - base tautomeric equilibrium.
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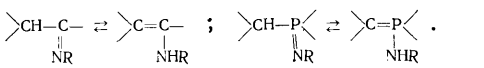
I. INTRODUCTION

By phosphorus-carbon prototropic tautomerism, we understand the type of tautomerism in which the proton migrates between a carbon atom and a phosphorus-containing functional group. In principle, phosphorus-carbon tautomeric systems can be derived from their purely organic prototypes by replacing the group accepting a proton from the carbon atom by a phosphorus-containing group. Thus, the phosphoryl-hydroxy-ylide system can be derived from the keto-enol system:



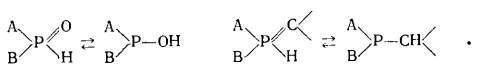
keto - enol phosphoryl - hydroxy-ylide

The phosphorimide–animoylide tautomerism can be derived similarly from the ketimine–enamine tautomerism:



Ketimine - enamine phosphorimide - aminoylide

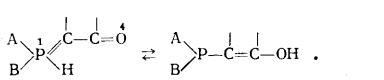
Furthermore, by virtue of the ease with which phosphorus changes its covalence from 3 to 4, diad-tautomeric systems of the type of dialkyl phosphites and their numerous analogues are widely known in the chemistry of organophosphorus compounds. By means of the reverse analogy, involving the replacement of the heteroatom linked to phosphorus by a carbon atom, it is possible to derive the diad phosphorus–carbon tautomerism:



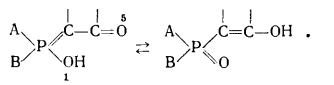
dialkyl phosphite tautomerism diad phosphorus - carbon tautomerism

It can be shown that all types of the phosphorus-carbon tautomerism constitute a single group of equilibria, a common feature of which is the transfer of a proton from the α-carbon atom to a phosphorus-containing functional group (Table 1).

Apart from the phosphorus-carbon diad and triad tautomeric systems, there is also a possibility of their vinylogue systems. Here, one can include, for example the tetrad system in which there is a proton 1,4-migration and not a 1,2-migration (diad migration):



Mention can also be made of a pentad system in which the proton is transferred from the 1-position to the 5-position:



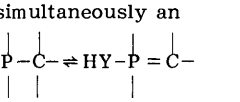
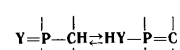
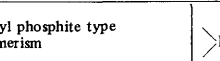
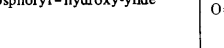
Although formally these systems do not fit the definition quoted above (in the last system, for example, the proton is transferred from the oxygen atom of the phosphorus-containing functional group to the oxygen atom of the carbonyl group, the keto-form is in this instance simultaneously an ylide form and the type of transition  is retained for the phosphorus atom, which makes it possible to classify these complex systems conventionally as of the phosphorus–carbon type. Furthermore, as will be shown below, there is always a typical phosphorus-carbon 1,2- or 1,3-transition in such systems together with the pentad or tetrad transitions from an oxygen or phosphorus atom to an oxygen atom and conversely.

Table 1. A schematic arrangement of the phosphorus–carbon prototropic systems.



Y	Type of tautomerism	General formula
Electron pair	diad, dialkyl phosphite type of tautomerism	
O	triad, phosphoryl - hydroxy-ylide	
S	triad, thiophosphorly-mercaptoylide	
RN	triad, phosphorimide-aminoylide	
C	triad, carbon - phosphorus - carbon	

The position of any prototropic tautomeric equilibrium is known to be determined by the relative acidities of the different forms under the given experimental conditions, i.e.

$$K = c_1/c_2 = K_2/K_1 ,$$

where c_1 and c_2 are the concentrations of forms 1 and 2 and K_1 and K_2 are their dissociation constants. In practice, a tautomeric equilibrium is observed in those cases where the dissociation constants of the forms differ by not more than 1–3 orders of magnitude (naturally this limit depends on the sensitivity of the method of analysis or calculation adopted for the tautomeric system). On the other hand, if the difference between the dissociation constants is large, the equilibrium is displaced almost completely towards the form whose dissociation constant is smaller.

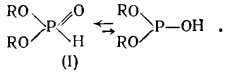
If this criterion is applied to typical phosphorus-carbon systems, namely the diad $\backslash CH-P/$ or triad $\backslash CH-P(=O)-$ systems it is clear that conversion into the ylide forms $\backslash C=P-H$ or $\backslash C=P-OH$ will occur only if the acidity of the CH forms becomes comparable to or greater than the acidity of the PH or OH forms. At the same time it is known that the PH acidity and especially the OH acidity is usually higher than the CH acidity. For the CH acidity to become equal to or greater than the acidity of the XH forms, a sufficiently powerful acidifying influence of groups attached to the carbon atom is necessary. Ylide forms can therefore be observed in those cases where strongly electronegative groups such as COR, SO_2R, CN, etc. are attached to the α-carbon atom. Naturally, the ratio of the acid properties of the forms depends on many intermolecular and external factors. However, to a first approximation it may be sufficient to estimate the acidifying influences of the substituents attached to the carbon and phosphorus atoms. Such an approximate approach has helped to discover certain new types of tautomerism to which this review is devoted.

II. THE DIAD PHOSPHORUS-CARBON TAUTOMERISM

As already mentioned, the diad phosphorus-carbon system is structurally related to other diads: phosphorus-oxygen, phosphorus-sulphur, and phosphorus-nitrogen. Some important information about these systems is therefore initially presented below.

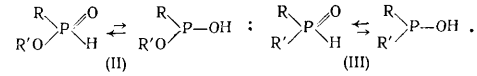
1. The Phosphorus-Oxygen, Phosphorus-Sulphur, and Phosphorus-Nitrogen Diads

Among all the types of diad tautomeric systems known in organic chemistry, the organophosphorus diads have been investigated to the greatest extent. They include in the first place dialkyl phosphites (I), the study of the tautomerism of which was initiated by A.E.Arbuzov[1] more than 75 years ago:



(I)

Although the conclusion that such tautomerism occurs had been reached a long time ago[2], proof of the existence of the hydroxy-form was obtained much later in kinetic isotope investigations[3,4]. Naturally, alkyl alkylphosphonites (II) and dialkylphosphonites (III) are included here also:

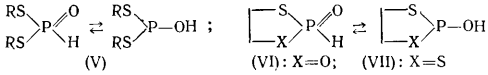


(II) (III)

In all the compounds of this type the tautomeric equilibrium is displaced towards the form with tetracoordinate phosphorus. Only in the case of bis(trifluoromethyl)phosphinite (IV) is the form with a tervalent phosphorus atom the only one present[5]:

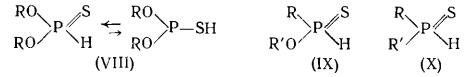
(IV)

It was later stated in the literature that the *S,S*-dialkyl phosphorodithioites (V) as well as the cyclic phosphorothiolites (VI) and (VII) are tautomeric mixtures of two forms[6–8]:



(V) (VI): X=O; (VII): X=S

O,O-Dialkyl phosphoromonothioites (VIII), the sulphur analogues of phosphites, were first investigated by the authors of this review at the beginning of the 1950's.[9] Here too the tautomeric equilibrium is displaced towards the thione forms under the usual conditions; the *O*-alkyl phosphonothioites (IX) and dialkylphosphinothioites (X) behave similarly:

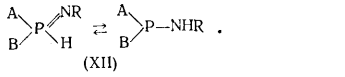


(VIII) (IX) (X)

According to an estimate, this equilibrium is displaced to an even greater extent than in dialkyl phosphites and only bis-(trifluoromethyl)phosphinothioite (XI) exists solely in the thiol form[10]:

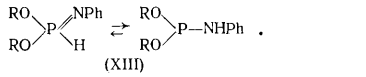
(XI)

The proportions of the different forms of phosphoramidites and their analogues (XII) are different:



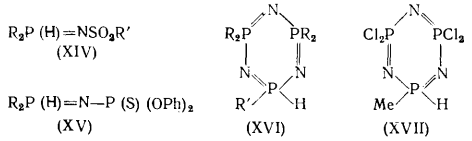
(XII)

Under the usual conditions, where A, B, and R are alkyl, aryl, or alkoxy-groups, the tautomeric equilibrium is displaced towards the amine form with a tervalent phosphorus atom[11]. This was first demonstrated by Kabachnik and Gilyarov[12] in relation to dialkyl N-phenylphosphoramidites (XIII).



(XIII)

In contrast to the oxygen and sulphur diads, in the case of phosphoramidites the second, i.e. the PH form could be detected for a much larger number of examples—for compounds (XIV),[13] (XV),[13] (XVI),[14] and (XVII):[15]



(XIV) (XV) (XVI) (XVII)

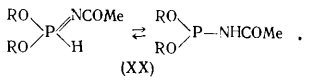
Instances of the tautomeric equilibria involving both forms have also been found[16,17]:

$$(RO)_2P(H)=N-SiMe_3 \rightleftarrows (RO)_2P-NH-SiMe_3 \ ;$$
(XVIII)

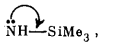
$$[Me_2N]_2P(H)=N-COMe \rightleftarrows [Me_2N]_2P-NH-COMe \ .$$
(XIX)

The PH forms of dialkyl phosphites (I) and their sulphur analogues (VIII) have much weaker acid properties than the OH and particularly the SH forms. The equilibrium is therefore as a rule displaced towards the PH forms. Only the introduction of two trifluoromethyl or cyclic ethylenedithiol groups at the phosphorus atom can increase the acidity of the PH form so much that it exceeds that of the OH or the SH forms, in the direction of which the equilibrium is in fact displaced[18].

The acidity of the NH forms of phosphoramidites and their analogues (XII) is lower than that of the PH forms; accordingly, the NH forms predominate in the equilibria. However, the difference between the acidities of the forms is not so great in this instance; when suitable substituents at the nitrogen and phosphorus atoms are used, it is easy to alter the relative acidities of the forms and thus influence the equilibrium position. For example, it is known that the equilibrium (XX) is displaced towards the amino-form[19]:


(XX)

However, if the strongly electron-accepting alkoxy-groups at the phosphorus atom are replaced by the more electron-donating dialkylamino-groups [see (XIX)], then the acid properties of the P–H bonds are diminished and the PH and NH forms can be detected in the tautomeric equilibrium[17]. On the other hand, if the trimethylsilyl group [see (XVIII)] is introduced at the nitrogen atom of the system (XX), then, as a result of the effect of the p–d conjugation



the nitrogen atom acquires a partial positive charge, the acidity of the N–H bond increases, and both forms again appear in the tautomeric equilibrium, which has been observed experimentally[16].

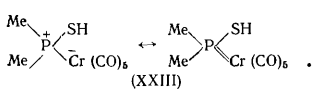
There are indications in the literature that the OH form of a dialkyl phosphite can be stabilised by incorporating it in a complex with a transition metal ion. For example, the complex (XXI), discovered in 1944 by Grinberg and Troitskaya[20,21]:

$$Pt\{P(OEt)_2OH\}_2 \cdot \{P(OEt)_2O\}_2 \ .$$
(XXI)

One can also refer to the complex $Mo(CO)_5[Ph_2POH]$ [22] and a number of others[23]. Dialkyl phosphorothioites form similar complexes in the SH form, for example, compound (XXII):[24,25]

$$Cr(CO)_5[Me_2PSH] \ .$$
(XXII)

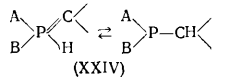
However, in discussing these and analogous complexes one must not forget that, instead of the free (solvated by solvent molecules) tautomeric forms with a tervalent phosphorus atom, one is dealing with compounds of another type [compounds (XXIII)], containing a tetracoordinate phosphorus atom:


(XXIII)

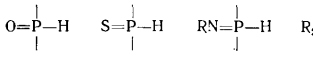
It is therefore illegitimate to consider examples such as those of "stabilisation" of phosphites with tervalent phosphorus.

2. Phosphorus–Carbon Diad Systems

As mentioned above, the phosphorus-carbon diad system (XXIV) is the carbon analogue of the dialkyl phosphite diad:

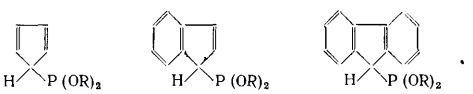

(XXIV)

This is the last of the four possible phosphorus diads:



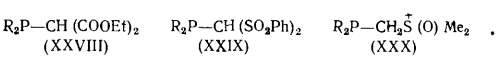
(a) The phosphorus–carbon diads existing in the CH form. Dialkyl phosphonites $(RO)_2P-CHR'_2$, alkyl phosphinites $(RO)R'P-CHR''_2$, and tertiary phosphines $R_2P-CHR'_2$ containing an α-hydrogen atom belong in the first place to phosphorus–carbon diad systems. However, they had not been considered previously from the standpoint of the possibility of the the diad phosphorus-carbon tautomerism. Indeed, these substances are always represented in the CH forms with a tervalent phosphorus atom since the acid properties of the C–H bond are still less marked than those of the N–H bond, the shift of the equilibrium towards the CH forms is even greater in this instance. Very powerful influences on the C–H and P–H bonds are necessary for the appearance of the experimentally detectable phosphinomethylene PH form.

Attempts to achieve such an influence on the CH acidity of phosphonites and tertiary phosphines have been made. Thus one of the authors of the present review and Tsvetkov[26] investigated for this purpose cyclopentadienylphosphonites (XXV), indenylphosphonites (XXVI), and fluorenylphosphonites (XXVII).


(XXV) (XXVI) (XXVII)

However, these substances proved to be pure CH forms.

Kolodyazhnyi, Gololobov, and co-workers introduced at the α-carbon atom of the R_2PCH group two alkoxycarbonyl groups [compound (XXVIII)],[27,28] two sulphonyl groups [compound (XXIX)],[29] the protonated dimethyl sulphoxylide group [compound (XXX)],[30] and certain others:


(XXVIII) (XXIX) (XXX)

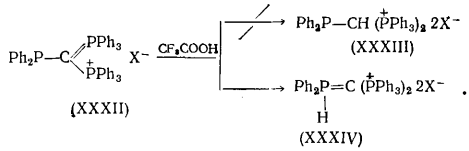
In all cases the groups R consisted of the simplest (unbranched) alkyl, phenyl, or alkoxy-groups. Only the CH forms of all these compounds could be detected in solutions by infrared spectroscopy, ^1H NMR, and NMR.[28] It has been stated[31] that the PH form of the phosphorylated acetaldehyde (XXXI) can exist in equilibrium with the CH and enol forms:

$$Ph_2P-CH_2-C(H)O \rightleftarrows Ph_2P-CH=CH-OH \rightleftarrows Ph_2P(H)=CH-C(H)O \ .$$
(XXXI)

However, the aldo-enol equilibrium has been demonstrated experimentally in this instance but the existence of a PH ylide form has been merely postulated.

(b) The phosphorus–carbon diad existing in the PH form. The first compound with the PH ylide structure was described in 1966 by Birum and Matthews[32]. When the phosphorany idene phosphonium salt (XXXII) was treated with trifluoro-

acetic acid, the formation of the ylide (XXXIV) with a P–H bond was observed:



(XXXII) (XXXIII) (XXXIV)

Two triphenylphosphonium groups attached to the central carbon atom proved to have such a powerful acidifying effect on the C–H bond in compound (XXXIII) that the proton added to the phosphorus atom with formation of the PH ylide (XXXIV) and not to the carbon atom.

Indeed, the triphenylphosphonium group belongs to the class of the most highly acidifying groups. In the study of the influence of this group on the tautomeric keto-enol equilibrium, we found[33] that its effect is significantly greater than that of, for example, the ethoxycarbonyl group, as can be seen from the following data: $MeCOCH_2COOEt$ (7% of enol); $MeCOCH(COOEt)_2$ (69% of enol); [34] $MeCOCH(COOEt)\overset{+}{P}Ph_3X^-$ (100% of enol). In the latter case, total enolisation is observed not only in solutions but also in the crystalline state[33,35].

According to Issleib and Lindner[36], the triphenylphosphonium group is at the head of the series of substituents Y arranged in order of their decreasing acidifying influence on the CH acidity of the phosphonium salts $Ph_3\overset{+}{P}CH_2YX^-$:

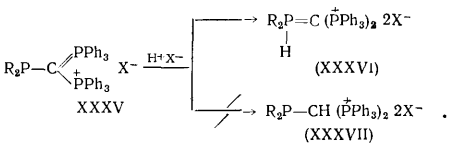
$$Ph_3P^+ > PhCO > MeCO > CN > COOR > P(S)R_2 \approx P(O)R_2 > PPh_2 > Ph > H > Me .$$

In terms of the Hammett constants, the phosphonium groups are also among those with the most pronounced electron-accepting properties ($\sigma > 0.9$).

The authors of this review have made a detailed study of the protonation of substances of the type of compound (XXXII). The substituents at the tervalent phosphorus atom were varied in such a way that their σ^{ph} constants, characterising the acidifying effect of the groups at the phosphorus atom, gradually diminished[37]:

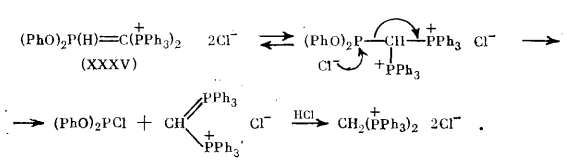
R	PhO	EtO	Ph	Me	Et	Bu
σ^{ph}	−0.06	−0.21	−0.59	−0.96	−1.10	−1.22

Phosphino-substituted phosphoranylidenephosphonium salts (XXXV) were protonated in various solvents by different acids (in an atmosphere of dry argon). According to $^{31}P\{^1H\}$ NMR data, only protonated PH forms (XXXVI) are formed in all cases[38]:



XXXV (XXXVI) (XXXVII)

These forms are characterised by a high constant J_{PH} = 450–700 Hz and other features (Table 2). All attempts to detect the CH form (XXXVII) in solution were unsuccessful. However, evidence has been adduced in support of the decomposition of compound (XXXV) with R = PhO under the influence of acids via the CH form[39]:



X-Ray diffraction analysis of compound (XXXVI, R = Bu, X = Br)[40] confirmed its structure (Fig. 1). The central carbon atom C(1) in this compound is markedly sp^2-hybridised (the sum of the angles between the bonds involving the carbon atom and the three phosphorus atoms is 359 °C), while the P(3) phosphorus atom is sp^3-hybridised, which undoubtedly indicates a PH structure.

Table 2. Parameters of the ^{31}P NMR spectra of the products (XXXVI) obtained by the protonation of the salts $R_2P^{\alpha}C[=P^{\beta}Ph_3]P^+Ph_3X^-$ (XXXV) by trifluoroacetic acid or hydrogen chloride in $CHCl_3$ or CH_2Cl_2.[38]

R	Solvent, reagent	δP^{α} (t), p.p.m.	δP^{β}(d), p.p.m.	J_{PP}, Hz	J_{PH}, Hz
Ph	CF_3COOH	8.6	25.3	22	500
Me	CF_3COOH	−1.1	25.8	19	525
Me	CH_2Cl_2, HCl	−2.1	24.5	21	525
Et	$CHCl_3$, HCl	22.5	24.7	21	460
Bu	CF_3COOH	17.2	25.4	17	450
Bu	$CHCl_3$, HCl	14.6	23.0	19	460
PhO	CH_2Cl_2, HCl *	54.5	21.5	29	698

* At −70 °C.

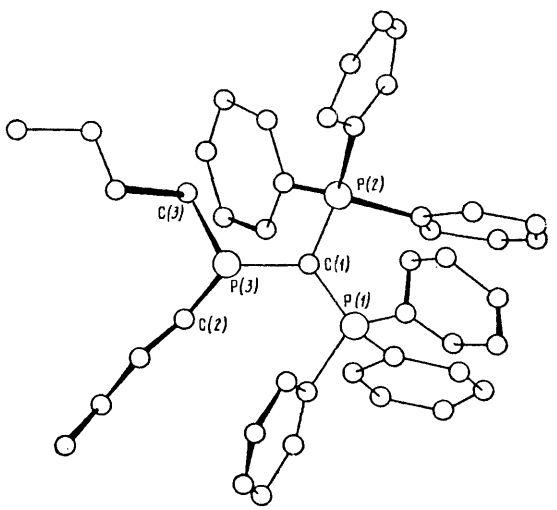


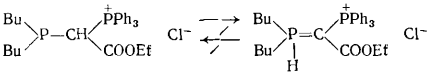
Figure 1. The structure of the $Bu_2P(H)=C(\overset{+}{P}Ph_3)_2$ cation. Angles: P(1)C(1)P(2) = 118°; P(2)C(1)P(3) = 117°; P(1)C(1)P(3) = 124°; C(1)P(3)C(2) = 115°; C(1)P(3)C(3) = 114°; C(2)P(3)C(3) = 109°; distances: C(1)P(1) = 1.69 Å; C(1)P(2) = 1.88 Å; C(1)P(3) = 1.72 Å.[40]

Certain PH ylides have been recently obtained by Kolodyazhnyi[41]. These are derivatives of phosphino-substituted malonic ester $RR'P(H)=C(COOMe)_2$, in which R = t-butyl and R′ are branched alkyl groups (for further details, see below).

(c) The phosphorus–carbon tautomeric diads. The starting point in the search for tautomeric phosphorus–carbon diad systems consisted of a comparison of the results of the

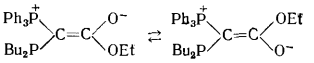
protonation of phosphino-substituted phosphoranylidenephosphonium salts (XXXV) and phosphino-substituted malonic esters (XXVIII). In the former case only the PH ylide (XXXVI) was found while in the latter only the CH acid (XXVIII) was discovered. In the former systems the CH acidity [of the (XXXVII) form] proved to be too high and the equilibrium was fully displaced towards the PH form (XXXVI). On the other hand, in systems of the second type the acidity of the CH form proved to be too small and the position of the phosphorus–carbon equilibrium was fully displaced towards this form. It was naturally postulated that, when one phosphonium and one ethoxycarbonyl group are introduced at the central carbon atom instead of two phosphonium groups [as in compound (XXXVII)] or two ethoxycarbonyl groups [as in compound (XXVIII)], one would expect the acidities of the two forms to be similar and that a true tautomeric equilibrium would result[42,43]. Naturally the equilibrium position should depend on the character of the substituents at the phosphorus atom because they also influence the relative acidities of the two forms.

The dibutylphosphinoethoxycarbonylmethylphosphonium salt (XXXVIII)



(XXXVIIIa) (XXXVIIIb)

proved to be a pure PH acid (XXXVIIIb). This ylide exists as a mixture of two conformers of the PH form, as shown by the doubling of the number of signals in the $^{31}P\{^1H\}$ NMR spectrum at a low temperature (Table 3). This kind of conformational isomerism of cisoid and transoid forms is already well known for unsubstituted alkoxycarbonylphosphinomethylenes[44,45]. It is also characteristic of the initial dibutylphosphinoethoxycarbonylmethylenephosphorane (XXXIX):



(XXXIX)

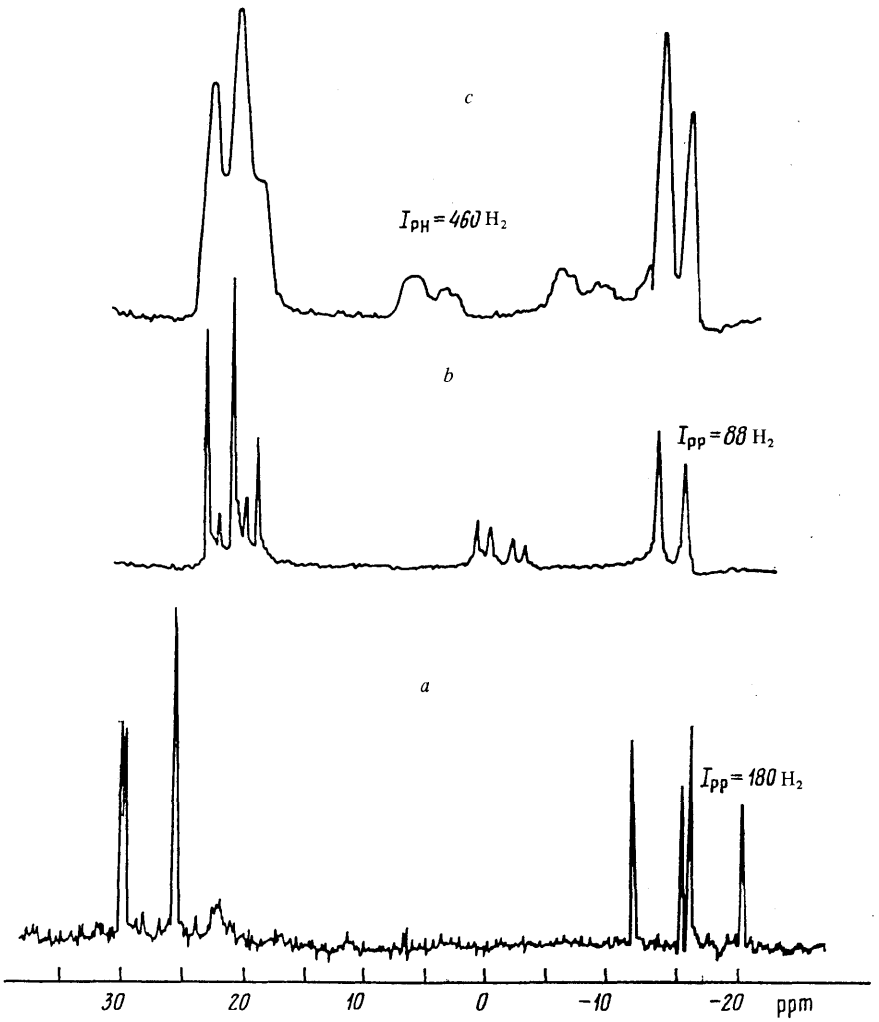
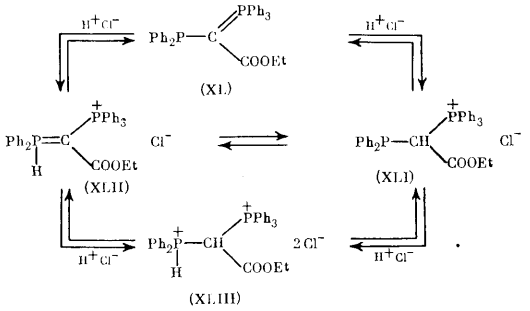


Figure 2. ^{31}P NMR spectrum of a solution of the $Ph_2PCH(\overset{+}{P}Ph_3)COOEt\ Cl^- \rightleftharpoons Ph_2P(H)=C(\overset{+}{P}Ph_3)COOEt\ Cl^-$ tautomeric mixture in CH_2Cl_2 at −80 °C: *a*) $^{31}P\{^1H\}$ NMR spectrum of the initial ylide; *b*) $^{31}P\{^1H\}$ NMR spectrum of the tautomeric mixture; *c*) ^{31}P NMR spectrum of the tautomeric mixture[42].

Consequently the acidity of the CH form again exceeded that of the PH form. However, the replacement of the two butyl groups at the tervalent phosphorus atom by two phenyl groups greatly increased the PH acidity and the protonated diphenylphosphinoethoxycarbonylmethylenetriphenylphosphorane proved to be a tautomeric substance. Its solution contains both the CH form (XLI) and the corresponding PH form (XLII). Overall, the acid-base and tautomeric transitions in this instance can be represented by the following scheme[40,42,43]:



The $^{31}P\{^1H\}$ NMR spectrum of the tautomeric mixture at −90 °C with the ratio ylide (XL) : HCl = 1 : 2 is fairly complex (see Table 3). It contains the signals of two conformers of the PH form (XLII) (four doublets at 21.4, 23.7, 0.5, and −2.4 p.p.m) and two doublet signals of the CH form (XLI) at −15.6 and 25.1 p.p.m. with $J_{PP} = 88$ Hz (Fig. 2).

Table 3. Parameters of the ^{31}P NMR spectra of the phosphinoylides $R_2P^{\alpha}C[=P^{\beta}Ph_3]COOEt$ and the products of their protonation with HCl.[40,42,43]

R	Compound	Solvent, reagent	t, °C	δpα (d) p.p.m.	δpβ (d), p.p.m.	J_{PP}, Hz	J_{PH}, Hz
Bu	(XXXIX), ylide	CH_2Cl_2	20	−33.1	27.3	156	—
Bu	(XXXIX), ylide	CH_2Cl_2	−80	−31.5	27.3	154	—
				−38.3	27.3	161	—
Bu	(XXXVIIIb), PH form	CH_2Cl_2, HCl	−80	5.7	19.4	32	460
				2.4	21.8	32	480
Ph	(XL), ylide	$CHCl_3$	20	−14.9	28.1	180	—
Ph	(XL), ylide	CH_2Cl_2	−70	−13.5	28.0	178	—
				−19.2	28.1	183	—
Ph	(XLII), PH form	CH_2Cl_2, HCl	−90	0.5	21.4	41.5	460
				−2.4	23.7	39.8	460
Ph	(XLI), CH form	CH_2Cl_2, HCl	−90	−15.6	25.1	88	—

The validity of the assignment of the signals with δ = 0.5 and −2.4 p.p.m. to the conformers of the PH form is indicated by the high splitting constant $J_{PH} = 460$ Hz observed when the suppression is removed. On the other hand, the assignment of signals with the splitting constant $J_{PP} = 88$ Hz to the CH form was confirmed by the study of the ^{13}C NMR spectrum of a solution of the pure CH form in a 10 : 1 CH_2Cl_2–CH_3CN mixture at −80 °C (see below). Under these conditions, the signal of the α-carbon atom with the chemical shift δ = 38.1 p.p.m. has a triple doublet splitting. The doublet splitting with $J_{CH} = 139.7$ Hz is due to the interaction with the added proton (CH group), the second doublet splitting with $J_{CP} = 57.0$ Hz is caused by the interaction with the phosphonium atom, and the third doublet splitting with the constant $J_{CP} = 48.0$ Hz is associated with the spin-spin coupling with the tervalent phosphorus atom. Only in the case of the CH form is it possible to observe such triple doublet splitting of the signal in the ^{13}C NMR spectrum.

With increase in the HCl concentration, there is initially a change in the relative signal intensities, indicating an increase of the concentration of the CH form (XLI), after which (in the presence of a large excess of HCl) the spectrum becomes greatly simplified and is converted into the spectrum of the doubly protonated form (XLIII) with a sharply reduced J_{PP} (to 7.3 Hz).

The position of the tautomeric equilibrium (XLII) ⇌ (XLI) depends on many factors. An increase of temperature favours the CH form (XLI). It has been found from the dependence of $\lg K_T$ on $1/T$ (Fig. 3) that the PH form is slightly more stable (by 0.65 kcal mol^{-1}) under these conditions than the CH form (Table 4); apparently an increase of the HCl concentration also acts like the increase of the polarity of the medium. It is of interest to note that only the CH form is present in the 10 : 1 CH_2Cl_2–CH_3CN mixture in the presence of two moles of HCl at −80 °C (see above).

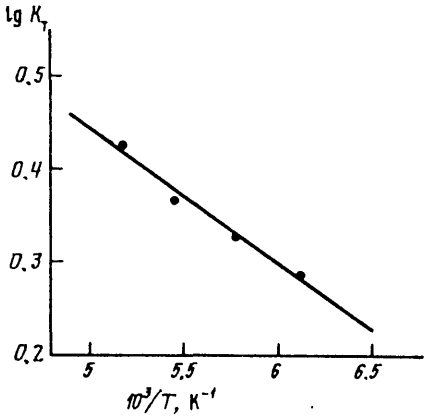


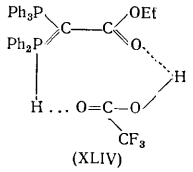
Figure 3. Temperature variation of the $Ph_2PCH(\overset{+}{P}Ph_3)_3COOEt\ Cl^- \rightleftharpoons Ph_2P(H)=C(\overset{+}{P}Ph_3)COOEt\ Cl^-$ tautomeric equilibrium constants.

Table 4. Dependence of the position of the tautomeric equilibrium between the PH and CH forms [(XLII) ⇌ (XLI)] on the solvent composition [−80 °C, (XL) : HCl = 1 : 2].[40]

Content of CH_3CN in CH_2Cl_2, %	Content of PH form, %	Equilibrium constant K_T = [PH]/[CH]
0	30	0.43
3.20	14	0.16
6.25	5	0.05
9.10	0	0

One PH form is observed in trifluoroacetic acid or in CH_2Cl_2 with an excess of CF_3COOH. It may be that trifluoroacetic acid stabilises the PH form, forming long hydrogen

bonds with the latter [see formula (XLIV)]:



(XLIV)

The next example of the phosphorus–carbon diad tautomerism was discovered somewhat later by Kolodyazhnyi[41]. It was noted above that the diphenylphosphino-derivatives of malonic ester (XXVIII) consist of 100% CH forms[27,28]. This applies also to the previously investigated derivatives of tervalent phosphorus (XXVIII) containing lower unbranched alkyl groups, the phenyl group, or an alkoxy-group at the phosphorus atom.

Continuing his persistent search for PH ylides, Kolodyazhnyi[41] investigated the analogous derivatives (XLV) and (XLVI) containing branched alkyl groups at the phosphorus atom, namely the t-butyl, s-butyl, isobutyl, and isopropyl groups, i.e. those characterised by the greatest $\pm I$ effect:

$$\underset{\text{(XLV)}}{RR'P{-}CH(COOMe)_2} \rightleftarrows \underset{\text{(XLVI)}}{RR'P(H){=}C(COOMe)_2}\ .$$

The study showed that in the crystalline state these substances are PH ylides (XLVI), where R = t-Bu, R' = iso-Pr, s-Bu, or Me_3SiCH_2. Their infrared spectra show only the absorption bands of the PH ylide. On fusion or dissolution of compounds (XLVI), bands appear in their infrared spectra in the region of 1700–1800 cm^{-1}, which are characteristic of saturated carboxylic acid esters and indicate the partial conversion of compound (XLVI) into (XLV). The ^{31}P NMR spectra also indicate the simultaneous presence of the PH ylide form (doublet with the constant J_{PH} = 435–440 Hz) and the CH form (singlet, δ = 12.5–35.5 p.p.m., depending on the nature of the alkyl groups). Integration of the signals in the NMR spectra and of the infrared bands made it possible to determine the constants K_T for the tautomeric equilibrium (XLVI) ⇋ (XLV). It was found that they depend not only on the character of the substituting groups at the tervalent phosphorus atom but also on the temperature and the nature of the solvent. It was observed that an increase of temperature shifts the equilibrium towards the CH form and the dependence of $\lg K_T$ on $1/T$ showed that the CH form is less favoured by energy factors (approximately to the extent of 2 kcal mol^{-1}). The influence of the solvent on the position of the tautomeric equilibrium is not very clear in this instance: the following series of solvents increasing the content of the PH form has been published[41]: C_6H_{14} < THF < C_6H_6 < CH_2Cl_2 < $CHCl_3$.

As regards the influence of the substituents at the phosphorus atom (Table 5), the author[41] assumes that the bulk of the substituting group plays a decisive role. He believes that bulky groups favour the formation of the planar system $HP{-}C^{-}(COOMe)_2$, which reduces the steric hindrance in structures (XLV) as a consequence of the interaction of the COOMe groups with the bulky substituents at the tervalent phosphorus atom. However, it is difficult to agree with his explanation. If one uses the data presented in Table 5, it can be readily seen that the (XLV) ⇋ (XLVI) tautomeric equilibrium constants obey satisfactorily the Hammett equation when one employs the constants σ_I^{Ph} characterising the influence of the groups attached to the phosphorus atom. The following values were then obtained for a solution in $CHCl_3$†: $\lg K_T^0 = -6.55$, $\rho = -2.351$, and $r = 0.979$ for $s = 0.14$ and $s_\rho = 0.25$ (Fig.4). On the other hand, if an attempt is made to set up a correlation between $\lg K_T$ and the Taft steric constants E_S, then the points cover the entire field of the graph and no reasonable relation can be seen.

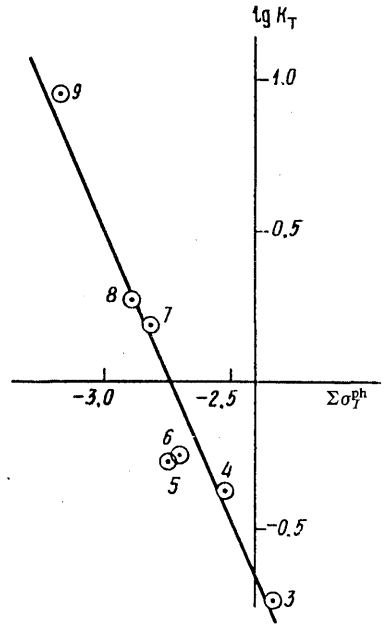


Figure 4. Dependence of the RR'PCH(COOMe)$_2$ ⇋ RR'P(H) = C(COOMe)$_2$ tautomeric equilibrium constants on $\sum \sigma_I^{ph}$ for the groups R and R' (the numbers of the points correspond to the number of the compounds in Table 5).

Table 5. The RR'PCH(COOMe)$_2$ ⇋ RR'P(H) = C(COOMe)$_2$ tautomeric equilibrium (20 °C, $CHCl_3$).[41]

№	R	R'	$\Sigma\sigma_I^{ph}$	Content of PH form, %	K_T
1	t-Bu	Me_2N	−1.28	0	0
2	t-Bu	Et_2N	−1.73	0	0
3	Bu	Bu	−2.44	15	0.18
4	iso-Pr	iso-Pr	−2.60	30	0.43
5	t-Bu	iso-Bu	−2.85	33	0.49
6	t-Bu	n-Bu	−2.79	35	0.54
7	t-Bu	iso-Pr	−2.85	61	1.56
8	t-Bu	s-Bu	−2.91	65	1.86
9	t-Bu	Me_3SiCH_2	−3.15	90	9.00

The parameters of the above correlation permit also other interesting conclusions. It is possible to calculate the position of the tautomeric equilibrium in the same systems but with other substituents at the phosphorus atom for which no

† The calculation was based on six points: 3,4, 6, 7, 8, and 9 (Table 5).

tautomeric relations had been observed earlier[27]. Such a calculation shows that in $CHCl_3$ the Et_2P group ($\sum\sigma^{ph} = -2.2$) should lead to an approximately 4% content of the PH form, the Ph_2P groups should give rise to less than 10^{-4}%, and the $(EtO)_2P$ group should produce an even smaller amount. This also applies to compounds with dialkylamino-groups: the content of the PH form should be ~0.3% for R = t-Bu and R' = Et_2N and ~0.08% for R = t-Bu and R' = Me_2N. Naturally the PH forms were not detected in solutions of these substances.

Thus the position of the diad prototropic equilibrium between the PH and CH forms in the series of phosphino-derivatives of malonic ester as well as the other instances investigated depends on the polar influences of the substituents which determine the acid strength of the CH and PH forms and thus the position of the tautomeric equilibrium.

In order to infer reliably the influence of the substituents at the α-carbon atom and at the phosphorus atom on the position of the proton, a quantitative approach to the estimation of the acidifying effect of these substituents is necessary. As mentioned above, one can use the constants σ_I^{ph} for the substituents at the phosphorus atom. The application of the Issleib and Lindner[36] series given above to the substituents at a carbon atom makes it possible to estimate the acidifying capacity of these groups only qualitatively. The authors of this review therefore recently developed a system of σ_C^- constants whereby one can carry out a correlation analysis of the dissociation constants of CH acids with a satisfactory accuracy[46]. This correlation system is naturally based on the Hammett σ^- constants and it was found that the numerical value of the constant depends on the number of substituents at the central carbon atom of the CH acid. Since there can be one, two, or three such substituents, each substituting group was characterised by three constants: $\sigma^-_{CH_3}$ for a primary carbon atom, $\sigma^-_{CH_2}$ for a secondary carbon atom, and σ^-_{CH} for a tertiary carbon atom#. The use of these constants made it possible to obtain excellent correlations of the pK_a for CH acids using the Hammett equation§. Thus it became possible to infer the acidifying influence of substituents on the strength of CH acids from the sum of the substituent constant σ_C^-¶. Table 6 lists certain constants σ_C^- characterising the acidifying influence of the groups at the carbon atom.

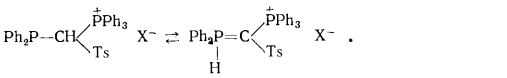
In conformity with the foregoing, for the above three types of compounds containing two identical groups at the phosphorus atom (phenyl or butyl), the sum $\sum\sigma^-_{CH}$ is 1.24 for the first type [compound (XXVIII)], 1.68 for the second type [compounds (XXXVIII) and (XLI)], and 2.16 for the third type [compound (XXXIII)]. The acidifying effect when the sum of the constants is 1.24 is insufficient for the transfer of a proton from C to P (it is insufficient for two phenyl groups at the phosphorus atom and almost insufficient for two butyl groups). The sum $\sum\sigma^-_{CH} = 1.68$ for two butyl groups gives rise to the PH structure (the CH acidity is then too great) and in the presence of two phenyl groups the CH⇌PH tautomeric system is produced. Finally, for the sum $\sum\sigma^-_{CH} = 2.16$, the proton is firmly held at the phosphorus atom (the CH acidity is too great).

Table 6. The $\sigma^-_{CH_2}$ and σ^-_{CH} constants characterising the acidifying influence of the groups on the CH acidity[46].

Group	$\sigma^-_{CH_2}$	σ^-_{CH}	Group	$\sigma^-_{CH_2}$	σ^-_{CH}
Me	0.12	0.13	COMe	0.88	0.66
Ph	0.365	0.26	COPh	0.98	0.78
p-$NO_2C_6H_4$	0.74	0.52	$PhSO_2$	0.77	0.71
COOMe	0.72	0.62	p-$MeC_6H_4SO_2$	—	0.70
COOEt	0.725	0.60	NO_2	1.26	1.12
CN	0.80	0.75	$Ph_3\overset{+}{P}$	1.22	1.08

One must bear in mind that the constants ρ of the correlation between the CH acidity and σ_C^- are fairly large (usually 10–25), which means that small changes in $\sum\sigma_C^-$ can give rise to large changes in the CH acidity.

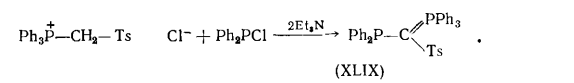
Next, studies were made on the (XLVII)⇌(XLVIII) systems with tosyl groups[47]:



(XLVII) (XLVIII)

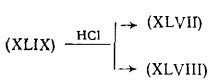
It was assumed that investigation would reveal either a tautomeric or an ylide system (XLVIII), since the sum of the constants $\sum\sigma^-_{CH} = 1.78$ is characterisitc of the form (XLVII), exceeding the corresponding sum (1.68) for the (XLI) ⇌ (XLII) tautomeric system (investigated previously) with an ethoxycarbonyl group at the α-carbon atom; however, it is significantly smaller than $\sum\sigma^-_{CH} = 2.16$ for the PH ylide diphosphonium structure (XXXVI).

The necessary compounds were synthesised in accordance with the scheme[47]



(XLIX)

Next, the ylide (XLIX) was protonated:



On treatment with trifluoroacetic acid or HCl in a slight excess, only the PH form (XLVIII) is observed. The $^{31}P\{^1H\}$ NMR spectrum (in a 3:1 $CHCl_3$–CH_2Cl_2 mixture) shows a typical AB quartet with $\delta_1 = -2.1$ p.p.m. and $\delta_2 = 19.8$ p.p.m. (with the constant $J_{PP} = 37$ Hz). When the suppression of the spin–spin coupling between the phosphorus and the protons is removed, the signal with $\delta = -2.1$ p.p.m. is converted into a characteristic doublet with $J_{PH} = 490$ Hz, which undoubtedly indicates the presence of the PH bond. Only the PH form

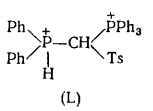
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A single reaction series can include terms with $\sigma^-_{CH_3}$, $\sigma^-_{CH_2}$, and σ^-_{CH}.

§ For the limitations of this correlation system, see Kabachnik and Mastryukova[45].

¶ Naturally, in estimating the CH acidity from the influence of the acidifying group, account must be taken also of the influence of the phosphorus-containing group. However, for many of these the values of σ_C^- are unknown and only comparisons for constant substituents at the phosphorus atom are therefore strictly legitimate.

(XLVIII) was observed also under other protonation conditions. Treatment with a large excess of HCl at −95 °C leads to the doubly protonated dication (L):

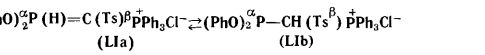


(L)

The positions of the signals in the ^{31}P NMR spectrum then change only slightly, but there is a sharp decrease of the spin-spin coupling constant: $J_{PP} = 6$ Hz (compared with 37 Hz for the monoprotonated compound). The dication is stable only at a low temperature and, on heating, the NMR spectrum of the dication is converted into that of the monocation (XLVIII).

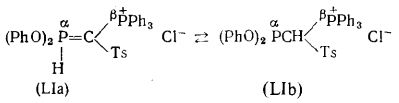
Thus the CH acidity induced by the presence of the triphenylphosphonium and tosyl groups proved to be too high and the proton migrated to the diphenylphosphino-group. However, when the phenyl groups at the tervalent phosphorus atom were replaced by phenoxy-groups, whose acidifying effect is incomparably greater ($\sigma_I^{ph} = +0.27$ for Ph and +2.83 for PhO), the PH acidity increased and an experimentally observable equilibrium between the two forms of (LI) again appeared (Table 7).

Table 7. ^{31}P NMR spectroscopic data (−80 °C, CH_2Cl_2) for the tautomeric system.



(LIa) (LIb)

Substance	$\delta_{P\alpha}$ (d), p.p.m.	$\delta_{P\beta}$ (d), p.p.m.	J_{PP}, Hz	J_{PH}, Hz
Initial ylide	173.2	16.4	14.6	—
PH form (LIa)	49.1	16.8	29.3	697
CH form (LIb)	149.5	20.0	7.4	—

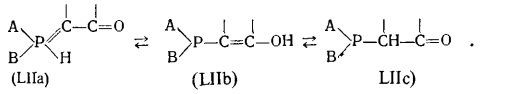


(LIa) (LIb)

The results obtained in the study of the diad phosphorus–carbon tautomerism can be summarised as follows. Table 8 lists the substituents X and Y at the carbon atom in order of decreasing acidifying capacity expressed by the sum of the constants σ_{CH}^{-}. The substituents at the phosphorus atom (on the left) are arranged from above downwards in order of increasing sum of the constants σ_I^{ph}, i.e. of increasing acidifying influence. Thus Table 8 lists on the left hand side the strongest CH acids and at the bottom the strongest PH acids. The upper left-hand corner represents the region of PH forms; here the carbon atom readily gives up a proton and the phosphorus atom readily accepts it. The lower right-hand corner represents the region of the CH form (the phosphorus atom readily gives up a proton and the carbon atom readily accepts it). The region of compounds with a distinct tautomeric equilibrium lies along the diagonal of Table 8. In this region the strengths of the CH and PH acids are similar and both forms are observed in the equilibrium.

3. The Tetrad Phosphorus–Carbon Tautomerism (A Vinylogue of the Diad Tautomerism)

As mentioned above, tetrad systems can be derived as vinylogues of the diad systems. The simplest examples of such tetrad tautomerism of compounds (LII) can be represented as a combination of the phosphorus-carbon diad and keto-enol tautomerisms:



(LIIa) (LIIb) LIIc)

The two tautomeric forms produced when the proton is fixed at the phosphorus atom [structure (LIIa)] and oxygen atom [structure (LIIb)] must be supplemented by the third form (LIIc), which can be produced when the proton is fixed at the α-carbon atom (as in diad tautomerism).

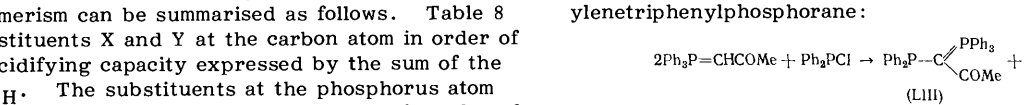
Table 8. The influence of substituents on the position of the tautomeric equilibrium*.

A, B	$\Sigma\sigma_I^{ph}$	X, Y; $\Sigma\sigma_{CH}^{-}$				
		$^{+}PPh_3$, $^{+}PPh_3$; 2,16	$^{+}PPh_3$, Ts; 1,78	$^{+}PPh_3$, COOEt; 1,68	COOMe, COOMe; 1,24	$^{+}PPh_3$, H; 1,22
t-Bu, s-Bu	−2.91	(PH)	(PH)	(PH)	CH⇄PH	(CH⇄PH)
Bu, Bu	−2.44	PH	PH	PH	CH⇄PH CH	(CH)
Ph, Ph	+0.54	PH	PH	CH⇄PH	CH	CH
PhO, PhO	+5.66	PH	CH⇄PH	(CH)	CH	CH

* Data expected on theoretical grounds are enclosed in brackets.

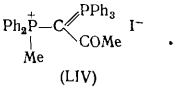
Diphenylphosphinoacetaldehyde (XXXI) (see above) could be regarded as a tautomeric substance of this kind if the existence of the PH ylide form could be demonstrated.

The products of the protonation of the diphenylphosphino-derivative of acetylmethylenetriphenylphosphorane (LIII) were investigated as the first tetrad system[48]. The phosphorane was obtained by the reaction of Ph_2PCl with acetylmethylenetriphenylphosphorane:



(LIII)

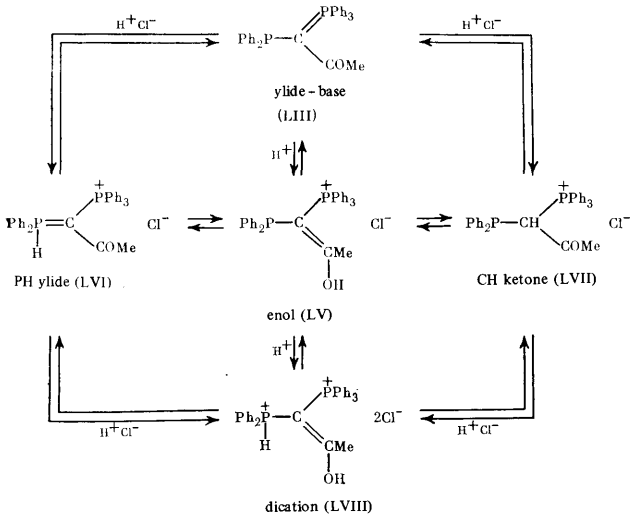
We may note that the spin-spin coupling constant in the $^{31}P\{^1H\}$ NMR spectrum of the ylide (LIII) is $J_{PP} = 184$ Hz (in CH_2Cl_2 at 20 °C). When the ylide (LIII) is methylated at the tervalent phosphorus atom, the product is the ylide (LIV) whose spectrum shows an AB quartet at 16.9 p.p.m. and 18 p.p.m. with $J_{PP} = 46$ Hz:



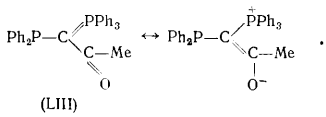
(LIV)

After extensive cooling, the multiplicity of the spectrum was found to be doubled owing to conformational isomerism.

The study of the prototropic transformations on protonation of the ylide (LIII) led to the following pattern of the acid-base and tautomeric transitions[48]:



The addition of a solution of HCl in CH_2Cl_2 to compound (LIII) at −80 °C in an argon atmosphere leads initially (in the presence of a small amount of the acid and immediately after its addition) to the enol form (LV). Its $^{31}P\{^1H\}$ NMR spectrum ($\delta_1 = -20.4$ p.p.m., $\delta_2 = 24.6$ p.p.m., and $J_{PP} = 144$ Hz) differs little from the spectrum of the ylide-base (LIII) ($\delta_1 = -18.8$ p.p.m., $\delta_2 = 25.2$ p.p.m., $J_{PP} = 184$ Hz). This is quite natural, because the electronic structure of the molecule of the initial ylide-base (LIII) differs little from that of the *O*-protonated form (LV):


(LIII)

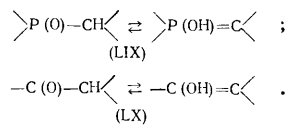
With increase of the HCl content in the reaction mixture (to 2 and 3 moles of HCl), six doublet signals with three splitting constants, equal in pairs, appear immediately. Two doublet signals are identical with those in the spectrum of the enol (LV) and therefore indicate its presence in the mixture; the other two doublets ($\delta = 2.6$ and 18.5 p.p.m., $J_{PP} = 51$ Hz) correspond to the PH form, since, after the removal of suppression the doublet at −2.6 p.p.m. splits into further two doublets with the constant $J_{PH} = 500$ Hz; furthermore, the splitting constant J_{PP} is in this case close to the constant found for the methylated derivative (LIV); the remaining two doublets refer to the CH form, which has been confirmed by repeated cross comparisons.

On further increase of the HCl concentration, the spectrum simplifies both as regards the positions of the signals (four doublets) and the character of J_{PP} and J_{PH}—it can be easily assigned to the dication (LVIII).

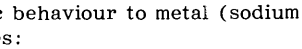
III. THE TRIAD PHOSPHORUS–CARBON TAUTOMERISM

1. The Phosphoryl–Hydroxy-ylide Tautomerism

The possibility of the phosphoryl–hydroxy-ylide tautomerism (LIX), which is analogous to the keto–enol tautomerism (LX), was first suggested by Arbuzov and Razumov in 1929 in connection with the discussion of the alkylation reactions of diethoxyphosphorylacetic acid ester[49]:

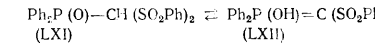

(LIX)
(LX)

In conformity with the views adopted at the time, they attributed a tautomeric behaviour to metal (sodium) derivatives of these substances:



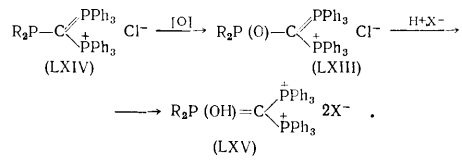
Arbuzov returned to this question in 1934 [50] and in 1947 [51], but naturally no evidence, apart from the dual reactivity of the alkali metal derivatives, was available at the time for the phosphoryl-hydroxy-ylide tautomerism.

A letter to the Editors by Kolodyazhnyi was published in 1976 [52] in which the tautomerism of phosphorylated di(benzenesulphonyl)methane (LXI)⇌(LXII) was reported:


(LXI) (LXII)

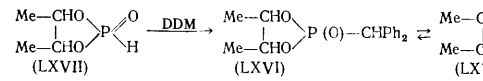
On acidification with hydrochloric acid, the sodium salt of compound (LXII) is converted into the free acid in the hydroxy-ylide form (LXII), whose structure was clearly confirmed by infrared spectroscopy. The acid crystallises from solution in benzene as the phosphoryl CH form (LXI) with an altered infrared spectrum. When the CH form is dissolved in $CHCl_3$, both forms are produced and their ratio varies with increase of temperature in favour of the phosphoryl CH form.

The authors of the present review and their co-workers[39] investigated simultaneously the protonation of phosphoryl-substituted phosphoranylidenephosphonium salts (LXIII) obtained by oxidising the corresponding phosphino-substituted salts (LXIV) with potassium permanganate; the formation of the hydroxy-ylide forms (LXV) was then observed:


(LXIV) (LXIII) (LXV)

When fluorosulphonic acid is protonated, the signals in the $^{31}P\{^1H\}$ NMR spectrum referring to the triphenylphosphonium phosphorus atoms do not undergo any significant changes, while the signals due to the phosphorus in the phosphoryl group undergo a downfield shift of 12.3 p.p.m. The protonation of phosphoryl groups is known to be accompanied as a rule by a similar change in the position of their NMR signal[53, 54].

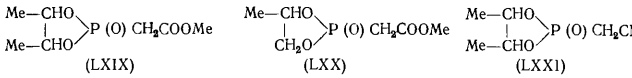
The next communication about the phosphoryl–hydroxy-ylide transitions was by Kazan chemists[55]. The authors reported that the cyclic diphenylmethylphosphonate (LXVI), obtained from the corresponding cyclic phosphite (LXVII) by reaction with diphenyldiazomethane (DDM) and subsequent oxidation, consists of the (LXVI)⇌(LXVIII) tautomeric mixture:


(LXVII) (LXVI) (LXVIII)

Unfortunately the authors did not present experimental data justifying this interesting and unexpected conclusion.

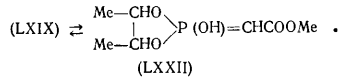
The phosphoryl–hydroxy-ylide tautomerism naturally obeys the same general laws which govern prototropic tautomerism in general. The conversion of a phosphoryl compound with an α-CH group into a hydroxy-ylide requires a powerful acidifying influence by the substituents at the central carbon atom which would equalise the strength of the CH acid with that of the P–OH acid, which is the hydroxy-ylide form. Here one must naturally take into account the influence of all the substituents—both at the carbon atom and at the phosphorus atom. From this standpoint, the butylenedioxyphosphinyl group in the CH acid (LXVI) should exert a powerful acidifying influence, while the influence of the phenyl group is moderately strong or even weak. The hydroxy-ylide form (LXVIII) contains at the phosphorus atom the butylenedioxy-group, which is a powerful electron acceptor. This form should be a fairly strong acid. Thus it would seem that one should expect the dominant form to be the phosphoryl CH form (LXVI), which is a weaker acid. On the other hand, if proton transfer nevertheless takes place despite the above reasoning, then one must accept that the influence of the butylenedioxy-group affects the CH acidity (LXVI) form to a much greater extent (increasing it sharply) than the OH acidity of the (LXVIII) form, which is enhanced to a lesser extent (a hypothesis which is in general unlikely). Further studies confirming the presence of the ylide form (LXVIII) are evidently necessary.

Other relations may be expected (and such are observed in reality) for the cyclic ethoxycarbonylmethylphosphonates (LXIX) and (LXX) or the corresponding nitriles (LXXI):



(LXIX) (LXX) (LXXI)

Here the methylene group has an environment analogous to that in the malonic ester and the manifestation of an appreciable CH acidity may be expected even in the absence of the dioxaphospholan ring; if the CH acidity becomes equal to or even approaches the OH acidity of the hydroxy-ylide form (LXXII) under the influence of the butylenedioxyphosphoryl group, then one can postulate the occurrence of the phosphoryl-hydroxy-ylide tautomerism (LXIX)⇌(LXXII), which is apparently actually observed[56]:

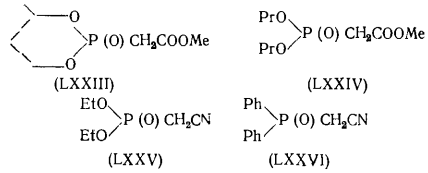


(LXXII)

Indeed the ^{1}H NMR spectrum of compound (LXIX) in CCl_4 contains the doublet signal of the P–CH_2 protons at 3.2 p.p.m. with the splitting constant $J = 21$ Hz, the doublet signal of the proton in the P=CH group at 2.9 p.p.m. with the same splitting constant, and the broad signal of the OH proton at 6.8 p.p.m.†

The ^{31}P NMR spectra also show the signals of the phosphoryl and hydroxy-ylide forms. In aqueous alcohol the equilibrium is fully displaced towards the ylide. The infrared spectrum confirms the ^{1}H NMR data. Analogous behaviour has been observed also for compounds (LXX) and (LXXI).

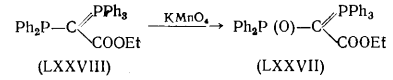
Five-membered cyclic methoxycarbonylmethylphosphonates proved to be strong acids ($pK_a = 2.71$–2.79 in 50% alcohol). The derivative of the six-membered dioxaphosphorinane (LXXIII), which has an analogous structure, is a weaker acid ($pK_a = 9.64$ and 11.05 for the two geometrical isomers), while the corresponding acyclic derivative (LXXIV) is weaker still ($pK_a = 12.10$). These substances are not tautomeric. The cyanides (LXXV) and (LXXVI) are likewise not tautomeric and their acid strengths are low ($pK_a = 11.58$ and 11.09 respectively):



(LXXIII) (LXXIV) (LXXV) (LXXVI)

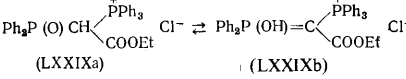
Thus in the presence of the usual acyclic substituents at the phosphoryl group, the acidifying effect of the methoxycarbonyl group COOMe ($\sigma^-_{CH} = 0.72$) and the cyano-group ($\sigma^-_{CH_2} = 0.80$) is insufficient to impart to the phosphoryl CH form an acid strength comparable to that of the hydroxy-ylide OH form, which is necessary for tautomeric behaviour. Only in the presence of an adjoining dioxaphospholan ring, as in compounds (LXIX)–(LXXI), is this condition fulfilled and prototropic transitions are observed. Incidentally, the nature of the influence of the dioxaphospholan ring is not clear (see above).

Tautomeric behaviour is to be expected when groups which cause a greater increase in the CH acidity are introduced at the α-carbon atom. This was achieved in a study by one of the present authors and his co-workers[57] after the simultaneous introduction of the triphenylphosphonium ($\sigma^-_{CH} - 1.08$) and ethoxycarbonyl ($\sigma^-_{CH} = 0.60$) groups at the α-carbon atom[57]. The synthesis of ethoxycarbonyldiphenylphosphinylmethylenetriphenylphosphorane (LXXVII) was achieved by oxidising the corresponding ethoxycarbonyldiphenylphosphinophosphorane (LXXVIII):



(LXXVIII) (LXXVII)

The phosphorane (LXXVII) is protonated by HCl with formation in solution of α-phosphorylated phosphonium salts having the CH structre (LXXIXa) and the OH structure (LXXIXb):[57]



(LXXIXa) (LXXIXb)

The salt forms crystals melting at 123–125 °C and containing the pure hydroxy-ylide form (LXXIXb) according to infrared spectroscopic data. The infrared spectrum showed a band at 1660 cm^{-1} due to the conjugated ethoxycarbonyl group (i.e. COOEt at a carbanionic centre) and a broad diffuse band due to the OH group (at 1500–2200 cm^{-1}). On dissolution in chloroform, an additional band appears in the infrared spectrum at 1730 cm^{-1} (non-conjugated ethoxycarbonyl group), which indicates the tautomeric equilibrium (LXXIXa)⇌(LXXIXb).

The ^{1}H NMR spectrum in CH_2Cl_2 contains the signals of both the CH form (LXXIXa) (a triplet at 1.12 p.p.m. and a quartet at 3.55 p.p.m. due to the protons of the exthoxy-group) and the signals of the OH form (LXXIXb) (a triplet at 0.49 p.p.m. and a quartet at 3.49 p.p.m due to the protons of the ethoxy-group; in both cases the spin-spin coupling constant $J_{HH} = 7$ Hz; in addition a broad singlet signal due to the proton of the OH group with $\delta = 10.7$ p.p.m. is observed. Evidently the signal of the CH proton is masked

† New data concerning the acid properties of compounds (LXIX) and (LXXIII) in ethanol have been published recently (O.Larsen and G.Aksnes, Phosphorus and Sulphur, 1983, 15, 219, 229). In contrast to the data quoted by Ovchinnikov et al.[56], compounds (LXIX) and (LXXIII) proved to be weak CH acids with virtually identical strengths (pK_a = 19.90 and 19.95).

in the case of the CH form by the signals of the aromatic protons). The ratio of the tautomeric forms (LXXIXa) : (LXXIXb) = 1 : 1.8 follows unambiguously from the ratio of the signal intensities[57].

The ^{31}P NMR spectra also confirm the above conclusion. They contain the signals of the two conformers of the OH form and the signals of the CH form:

	δ_1, p.p.m.	δ_2, p.p.m.	J_{PP}, Hz
OH form, conformer 1:	44.5 p.p.m.	19.1	41
OH form, conformer 2:	41.0	20.0	44
CH form	28.1	23.9	7

We may note that the low value of J_{PP} is characteristic of the structures of the type of (LXXIXa). The position of the tautomeric equilibrium in the system investigated depends on the nature of the solvent and the temperature[57].

An analogous study has been carried out for compounds similar to those described previously but with the replacement of the ethoxycarbonyl group by the tosyl group[58]. The phosphorane (LXXX) with the tosyl group has been synthesised by oxidising the phosphinophosphorane (LXXXI). Next, the entirely stable hydroxy-ylide (LXXXII) with m.p. 193 to 195 °C was obtained in 92% yield by treatment with HBr in ether:

$$Ph_2P{-}C(PPh_3)(Ts) \xrightarrow[(CH_2Cl_2,\ Me_2CO)]{KMnO_4} Ph_2P(O)C(PPh_3)(Ts) \xrightarrow[Et_2O]{HBr} Ph_2P(OH){=}C^{+}(PPh_3)(Ts)\ Br^-$$

(LXXXI) (LXXX) (LXXXII)

The structure of the bromide salt of the hydroxy-ylide was investigated by X-ray diffraction (Fig. 5). The central carbon atom C(1) has in this case a planar trigonal structure (its displacement from the plane towards the bromide anion is 0.118 Å) and the (C(1)–P(1) and C(1)–P(2) bonds are shortened (1.751 and 1.764 Å), compared with the single C–P bonds, which shows that they have a bond order of 1.5. The C–SO_2 bond is also somewhat shortened (1.728 Å compared with 1.772 Å for C_{ar}–S), which shows that the sulphur atom adjoins the anionic centre. Finally, there is the O...H...Br hydrogen bond with a length of 3.078 Å. The infrared spectrum of the crystalline ylide confirms its structure.

The situation does not change when the hydroxy-ylide (LXXXII) is dissolved in deuterochloroform. The ^1H NMR spectrum of the solution shows a singlet signal due to the CH_3 proton at 2.27 p.p.m. and a broad singlet signal of the OH proton at 11.2 p.p.m., the ratio of the integral intensities is 3 : 1, which indicates the absence of the CH form of compound (LXXXIII):

$$(LXXXII) \rightleftharpoons Ph_2P(O)CH(PPh_3)(Ts)\ Br^-$$

(LXXXIII)

The ^{31}P NMR spectrum shows only two doublet signals at 18.2 p.p.m. and 46.4 p.p.m. with the splitting constant J_{PP} = 29 Hz. Tautomerism of the type (LXXXII) ⇌ (LXXXIII) is not observed[58].

Thus the combination of the triphenylphosphonium and ethoxycarbonyl groups leads to the phosphoryl–hydroxy-ylide tautomerism and the replacement of the ethoxycarbonyl group by the tosyl group shifts the tautomeric equilibrium completely towards the hydroxy-ylide form in both the crystalline state and in solutions. An explanation of this phenomenon should be sought in the stronger acidifying influence of the tosyl group ($\sigma^-_{CH} = 0.70$) compared with the ethoxycarbonyl group ($\sigma^-_{CH} = 0.60$) on the CH acidity. The difference of 0.10 of a unit between the values of $\sum\sigma^-_{CH}$ combined with the steep slope of the relation between the CH acidity and $\sum\sigma^-_{CH}$ naturally increase sharply the CH acidity of the (LXXXIII) form and thus fully displace the equilibrium in the direction of the (LXXXII) form.

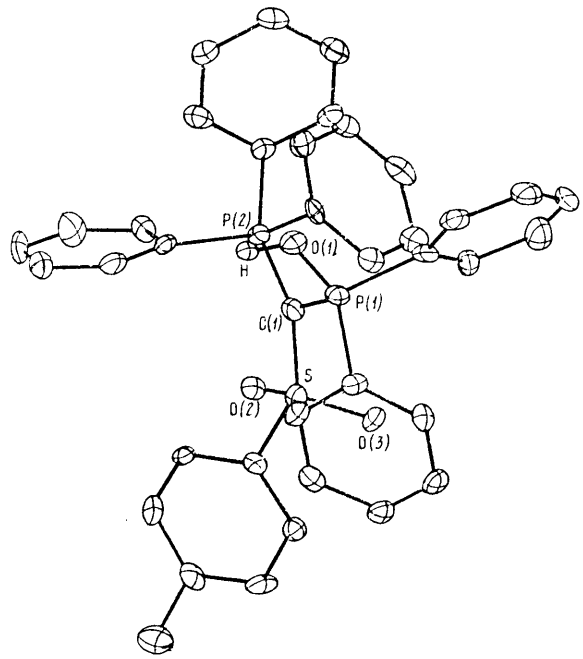


Figure 5. The structure of the cation of the bromide salt $Ph_2P(OH){=}C^{+}(PPh_3)Ts\ Br^-$; angles: P(1)C(1)P(2) = 122°; P(1)C(1)S = 121°; P(2)C(1)S = 115°.[58]

As shown above, a single alkoxycarbonyl group ($\sigma^-_{CH_2} = 0.72$) at the central carbon atom is insufficient for the tautomeric transfer of a proton to the oxygen atom of the phosphoryl group; the combination of the alkoxycarbonyl group with the triphenylphosphonium group ($\sum\sigma^-_{CH} = 1.68$) proved to be entirely sufficient for the manifestation of the tautomeric transition; on the other hand, the combination of the triphenylphosphonium group with the tosyl group ($\sum\sigma^-_{CH} = 1.78$) and also the combination of two triphenylphosphonium groups ($\sum\sigma^-_{CH} = 2.16$) lead to a "redistribution" of the CH acidity: the tautomeric equilibrium proved to be displaced in the direction of the hydroxy-ylide form.

It was therefore of interest to investigate the influence of two tosyl groups ($\sum\sigma^-_{CH} = 1.40$) at the central carbon atom in the structures (LIX) considered. Two tosyl groups should lead either to the CH form or to tautomerism between the CH and OH forms. This question has been recently elucidated by Kolodyazhnyi[60], who investigated the influence of the substituents X on the position of the tautomeric equilibrium in the

(LXXXIV)⇌(LXXXV) system:

$$Ph_2P(O)-CH(SO_2C_6H_4X)_2 \rightleftarrows Ph_2P(OH)=C(SO_2C_6H_4X)_2$$
(LXXXIV) (LXXXV)

In a pure state these substances consist of colourless crystals, which are very stable in air. They have the structure of the CH forms (LXXXIV), as can be seen from their infrared spectra, which contain bands at 1200–1210 cm^{-1} (P=O), 1160 to 1170 cm^{-1} (sym.SO_2), 1340–1350 cm^{-1} (asym.SO_2), and 2820 to 2840 cm^{-1} (CH). They are all strong acids (Table 9). However, in solution both forms, (LXXXIV) and (LXXXV), are present, differing in the chemical shifts in their ^{31}P NMR spectra (these are 21–24 p.p.m. and 47–49.5 p.p.m. respectively). The protons of the CH and OH groups are not manifested in the ^1H NMR spectra at the usual temperature but they can be detected on cooling—the signals of the OH protons are at 10–11 p.p.m. and those of the CH protons at 6–7 p.p.m. These are doublet signals (J_{PH} = 13 Hz); at −7.5 °C they lose the doublet structure and at +30 °C they disappear.

Table 9. The influence of substituents X on acidity and the tautomeric equilibrium[60].

$Ph_2P(O)-CH(SO_2C_6H_4X)_2 \rightleftarrows Ph_2P(OH)=C(SO_2C_6H_4X)_2$ [60]
(LXXXIV) (LXXXV)

X	σ_n	K_T (THF, 25 °C)	pK_a, (50% CH_3OH)
p-Cl*	+0.227	1.20	3.55
H	0	0.25	3.60
p-Me	−0.17	0.11	3.62
p-MeO	−0.268	0.04	3.68

* K_T = 1.32 at 20 °C and 1.98 at 30 °C.

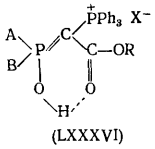
The infrared spectra of the solutions are also different for the CH and OH forms. The spectrum of the CH form (LXXXIV) shows bands at 1200 cm^{-1} (P=O), 1170 cm^{-1}, and 1350 cm^{-1} (SO_2 attached to an sp^3-hybridised carbon atom); the spectrum of the OH form (LXXXV) shows bands at 1300 cm^{-1} and 1290 cm^{-1} (SO_2 attached to an sp^2-hybridised carbon atom). Table 9 lists the (LXXXIV)⇌(LXXXV) equilibrium constants as a function of the substituent X. Using the data in Table 9, it can be shown that the tautomeric equilibrium constants obey satisfactorily the Hammett equation when the usual constants σ_p are used:

$$\lg K_T = -0.51 + 2.867\,\sigma_p \quad (r = 0.994;\ s = 0.08;\ s_p = 0.21).$$

An increase of temperature increases the relative content of the (LXXXIV) form, which indicates a greater stability of the hydroxy-ylide form (LXXXV). The equilibrium position depends on the nature of the solvent, the content of the (LXXXV) form increasing in the sequence

$$CH_2Cl_2 < CHCl_3 < CCl_4 < THF .$$

In conclusion of this section, mention must be made of the striking stability of the hydroxy-ylide forms. They are apparently stabilised by hydrogen bonds, which can be both intramolecular, as in structure (LXXXVI), and intermolecular:



(LXXXVI)

Apart from the oxygen atoms of the COOR or SO_2Ar substituents, halide ions can also function as proton acceptors in the hydrogen bonds. This problem has so far been little investigated, but the existence of the hydrogen bonds has been demonstrated. They reduce the acidity of the OH forms and hence displace the equilibrium in their direction.

2. The Thiophosphoryl–Mercaptoylide Tautomerism

This type of triad phosphorus–carbon tautomerism (LXXXVII)⇌(LXXXVIII) is the phosphorus analogue of the thioketo-enethiol tautomerism (LXXXIX)⇌(XC):

$$>P(S)-CH< \rightleftarrows >P(SH)=C< \qquad -C(S)-CH< \rightleftarrows -C(SH)=C< .$$
(LXXXVII) (LXXXVIII) (LXXXIX) (XC)

All the thiophosphoryl-compounds known previously, namely tertiary phosphine sulphides $R_2P(S)-CHR'R''$, phosphinothionates $(RO)R'P(S)CHR''R'''$, and phosphonothionates $(RO)_2P(S)CHR'R''$, are thione derivatives, i.e. correspond to structure (LXXXVII). Owing to the low basicity of the thiophosphoryl group (this is equivalent to a high acidity of its protonated form), a rarer appearance of the mercaptoylide form (LXXXVIII) than of the corresponding hydroxy-ylide form was to be expected for the thiophosphoryl-mercaptoylide system (LXXXVII)⇌(LXXXVIII). In other words, the transfer of a proton from the (LXXXVII) forms to the (LXVIII) forms requires a greater CH acidity of the (LXXXVII) forms than was the case for the phosphoryl-hydroxy-ylide transitions (see the previous section).

The first representative of a thiophosphoryl compound with the (LXXXVIII) structure was obtained[61] by the authors of this review and their co-workers. When the thiophosphorylated phosphoranylidenephosphonium salt (XCI) was protonated by fluorosulphonic acid, the mercaptoylide form (XCII) was obtained:

$$Me_2P(S)-C(PPh_3)(\overset{+}{P}Ph_3)\ X^- \xrightarrow{FSO_2OH} Me_2P(SH)=C(\overset{+}{P}Ph_3)(\overset{+}{P}Ph_3)\ 2X^- .$$
(XCI) (XCII)

S-Protonation was detected from the characteristic downfield shift of the signal in the $^{31}P\{^1H\}$ NMR spectrum by 7.2 p.p.m. (cf. Skvortsov et al.[54]).

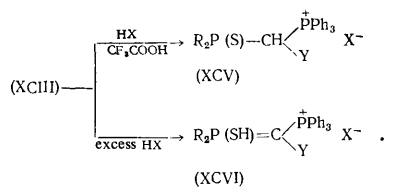
Later the same workers investigated the thiophosphoryl-mercaptoylide tautomerism in greater detail[62] and obtained unexpected results. Various thiophosphoryl-substituted phosphinomethylenes (XCIII) have been synthesised by adding sulphur to the corresponding phosphino-derivatives (XCIV):

$$R_2P-C(PPh_3)Y \xrightarrow{S} R_2P(S)-C(PPh_3)Y ;$$
(XCIV) (XCIII)

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)
R	Ph	Bu	EtO	PhO	Ph	Bu	Ph	Bu	Bu
Y	Ts	Ts	Ts	Ts	COOEt	COOEt	$\overset{+}{P}Ph_3Cl^-$	$\overset{+}{P}Ph_3Cl^-$	$\overset{+}{P}Ph_3Br^-$

These compounds were protonated by various acids under different conditions. Of the two types of protonation—at the sulphur atoms, as in structure (XCVI), and at the carbon

atom, as in structure (XCV)—only one type has been invariably observed as a function of the initial compound, the protonating agent, and the reaction conditions:



(XCV)

(XCVI)

Thus the protonation of compounds (XCIII, a–f) by hydrogen halides in equimolar proportions or in the presence of an excess of the latter leads only to the CH forms (XCV, a–f). The signal of the triphenylphosphonium phosphorus in the $^{31}P\{^1H\}$ NMR spectrum then undergoes a downfield shift by 1.5–7 p.p.m. and the constant J_{PP} diminishes significantly, amounting to 32–42 Hz before protonation and to 1–2 (at most 6) Hz after protonation, which is extremely characteristic of CH protonation. Frequencies corresponding to the SO_2 and COOEt groups attached to an sp^3-hybridised carbon atom are observed in the infrared spectrum. Apart from the signals due to the protons of the butyl, phenyl, and tosyl group, the ^1H NMR spectrum of the salt (XCVb) contains doublets with $\delta = 8.8$ p.p.m. and $J_{PCH} = 12.1$ and 13.6 Hz, which indicates unambiguously the CH structure (XCV). The ratio of the integral intensities of the signals of the CH proton and the CH_3 protons of the tosyl group is then 1 : 3. Protonation of the thiophosphorylylides (XCIII, e and f) by trifluoroacetic acid is also directed solely to the central carbon atom. The hydrochlorides (XCV, a–c), formed on protonation by HCl, are crystalline substances; they are all very strong acids which readily lose HCl on storage in air, the chlorides being less stable than the bromides.

Thus in this group of compounds the strength of the SH acids exceeds significantly that of the CH acids, although the latter are fairly strong.

A different behaviour is observed on protonation of compounds (XCIII, g–i), since this should entail the protonation of extremely strong acids. Indeed, on treatment of the thiophosphoryl ylides (XCIII, g–i) with HCl in CH_2Cl_2 (even with a large excess of HCl) or on treatment with an excess of trifluoroacetic acid, the addition of a proton is not always observed at the usual temperature. Only at temperatures between −70° and −85 °C in CH_2Cl_2 on treatment with an excess of hydrogen halide or on dissolution in fluorosulphonic acid is protonation observed, but in these instances only at the suphur atom.

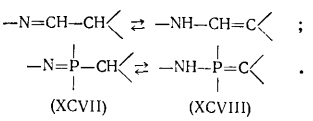
Thus, when compounds (XCIII, g and h) are treated with HSO_3F, doublet signals with the chemical shifts $\delta = 3.67$ p.p.m. for compound (XCVIg) and 3.05 p.p.m. for compound (XCVIh) and the splitting constants $J_{PSH} = 10$ and 8 Hz respectively appear in the ^1H NMR spectra. Spectra of this kind are very characteristic of thiophosphoryl compounds protonated by fluorosulphonic acid[63].

In the ^{31}P NMR spectra the signal of the thiophosphoryl phosphorus atom shifts downfield by 1–5 p.p.m. compared with the non-protonated compounds. The spin–spin coupling constant J_{PP} not only does not diminish under these conditions, as in the previous instance of C protonation, but actually increases somewhat.

Thus a system in which the (LXXXVII) and (LXXXVIII) forms are in an experimentally observed tautomeric equilibrium has been found for thiophosphoryl compounds of type (LXXXVII). If the acidity of the CH form is insufficient [the sum of the constants of the substituents at the central carbon atom $\sum\sigma^-_{CH} = 1.78$ for compounds (XCV, a–d) and, especially, 1.68 for compounds (XCV, e and f)], then only the CH form is produced. If the acidity of the CH form is high [$\sum\sigma^-_{CH} = 2.16$ for compound (XCVI, g–i)], then the proton is transferred to the sulphur atom and we detect exclusively the SH form. Apparently the region of the thiophosphoryl-mercaptoylide tautomerism involving thiophosphoryl compounds should occur for values of the sum of the constants $\sum\sigma^-_{CH}$ of the substituents at the central carbon atom between 1.78 and 2.16. The synthesis of thiophosphoryl compounds with such substituents at the α-carbon atom and the study of their thiophosphoryl-mercaptoylide tautomerism are matters for the future.

3. The Phosphorimide–Aminoylide Tautomerism

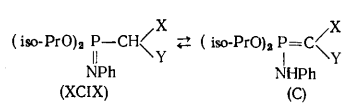
The phosphorimide–aminoylide tautomerism is the phosphorus analogue of the well known azomethine tautomerism:



(XCVII) (XCVIII)

Compared with previous cases—the phoshoryl-hydroxyylide tautomerism (LIX) and the thiophosphoryl–mercaptoylide tautomerism (LXXXVII) and (LXXXVIII)—there is not in this instance such a sharp difference between the polarities of the ends of the N = P = C triad; the relative acidities of the CH and NH forms can therefore change significantly under the influence of substituents at the nitrogen and carbon atoms. This type of tautomerism has been investigated by the Kiev chemical school[64–67]. Referring to it, in conformity with the nomenclature of the phosphorus-nitrogen compounds adopted in Kiev, as the phosphazo-ylide tautomerism, Kolodyazhnyi, Kukhar', Gololobov, and others investigated thoroughly both the methods of analysis of the tautomeric mixtures and the factors influencing the position of the phosphorimide-aminoylide equilibrium. It was established that the imide (XCVII) and iminoylide (XCVIII) forms can be clearly distinguished by means of infrared spectra and also ^1H and ^{31}P NMR. Thus, when there are two COOR groups at the carbon atom of the (XCVIII) form, the ^{31}P NMR spectrum shows a signal in the vicinity of 50 p.p.m., while for the corresponding (XCVII) form the signal is at 0 p.p.m. The ^1H NMR spectra of the (XCVII) forms contain a doublet due to the CH group in the range 3.5–4 p.p.m., while the spectra of the (XCVIII) forms contain the doublet of the NH group at 7–13 p.p.m. In the infrared spectra the vibration frequency of the COOR group at the α-carbon atom depends on the state of hybridisation of the latter and amounts to 1700–1760 cm^{-1} for the sp^3 hybridisation and to 1600–1700 cm^{-1} for the sp^2 hybridisation.

Thus the presence or absence of the tautomeric equilibrium has been established and in many instances its constants have been determined. The sharp influence of substituents at the nitrogen and carbon atoms on the equilibrium is noteworthy. Thus, in the presence of two isopropoxy-groups at the phosphorus atom, i.e. in the (XCIX) ⇌ (C) system



(XCIX) (C)

the equilibrium position (in CCl_4 at 28 °C) changes as follows:

X, Y	$\Sigma\sigma_C^-$	Content of NH form, %
$(COOMe)_2$	1.24	100
COOMe, Ph	0.88	0
COOMe, H	0.72	0

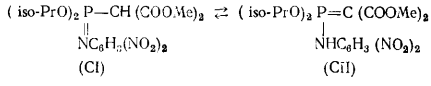
If the NH acidity is reduced by replacing the phenyl group at the nitrogen atom by the methyl group, then 100% of the NH form will be present not only in the first case for $\sum\sigma_C^- = 1.24$ but also for $\sum\sigma_C^- = 0.88$; even for $\sum\sigma_C^- = 0.72$, its content will still be 90%. On the other hand, if the NH acidity is increased by introducing the 2,4-dinitrophenyl group at the nitrogen atom instead of the phenyl group, then in the first case ($\sum\sigma_C^- = 1.24$) only 30% of the NH and not 100% is observed and, finally, the greatest increase of the NH acidity, resulting from the introduction of the tosyl group at the nitrogen atom, leads to the complete disappearance of the NH form in all the three instances considered. Thus the results obtained by the Kiev chemists[64-67] can be readily interpreted from the standpoint developed in the present review.

The nature of the solvent has an appreciable influence on the phosphorimide–aminoylide equilibrium. The content of the aminoylide form increases in the following series of solvents from left to right:

$$CCl_2{=}CCl_2 < CCl_4 < CH_3OH < CH_3CN < CHCl_3 \quad .$$

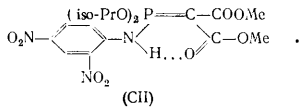
This series is apparently determined by the simultaneous operation of several factors.

An increase of temperature favours the imide form (XCVII). Thus the study of the temperature variation of the equilibrium in the (CI) ⇌ (CII) system



(CI) (CII)

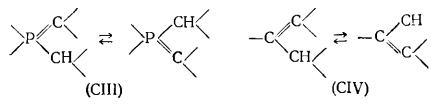
showed that $\Delta H = -5.9 \pm 0.5$ kcal mol^{-1} and $\Delta S = -21$ e.u. for a 0.2 M solution in CCl_4. The aminoylide form (CII) is energetically more favourable and more stable than the imide form (CI). The high entropy of the conversion of the ylide into the imide is noteworthy; this enabled the author of the study quoted above to postulate that the ylide form has a more rigid structure as a consequence of an intramolecular hydrogen bond:



(CII)

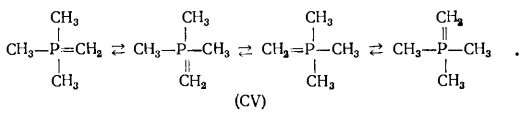
4. The Carbon–Phosphorus–Carbon Tautomerism

Here we are dealing with the phosphorus analogue (CIII) of the three-carbon tautomerism (CIV):



(CIII) (CIV)

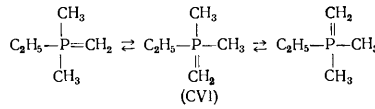
The first data on the degenerate tautomerism of this kind were published by Schmidbaur and Tronich[68], who found that the ^{1}H NMR spectra of solutions of trimethylmethylenephosphorane (carefully freed from impurities) depend on temperature and that at 100 °C the signals of the methyl and methylene protons merge owing to the degenerate tautomeric migrations of the proton in system (CV):



(CV)

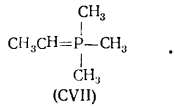
The activation energy for such transformations was estimated as 20 kcal mol^{-1}. The transformation is catalysed by added methanol, water, silanol, and in general proton donors. When traces of CH_3OH are introduced, a singlet signal is observed in the ^{1}H NMR spectrum already at −30 °C.

Tautomeric transitions (also degenerate) analogous to those of methylenetrimethylphosphorane have been observed for ethyldimethylmethylenephosphorane (CVI)[68]:



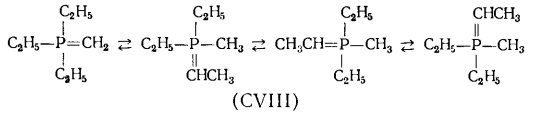
(CVI)

In the absence of catalysis by methanol, the ethyl group is not involved in the tautomerism, while the presence of methanol, the methylene protons of the ethyl group are involved in the merging of the signals, which indicates the appearance of the fourth tautomeric form (CVII), which is in equilibrium with the three previous forms:



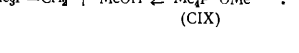
(CVII)

The ^{1}H NMR spectrum of the compound $(C_2H_5)_3P{=}CH_2$ undergoes no temperature-induced changes below 100 °C, but, after the addition of methanol, the equilibrium of the four forms in system (CVIII) is immediately established[68]:



(CVIII)

Strictly speaking the conversion of the first form specified into any one of the other three constitutes a non-degenerate tautomeric transition. However, the differences between the energy relations of the forms are in this instance very small and the system approaches a degenerate state. An analogous situation (with complete degeneracy) has been observed for triethylethylidenephosphorane $(C_2H_5)_3P{=}CHCH_3$, whose ^{1}H NMR spectrum is independent of temperature. The addition of only traces of methanol induces a rapid proton migration. As regards the mechanism of the catalytic action of methanol, it has been suggested that methanol reacts with the ylide to form phosphonium methoxide (CIX) by the reversible reaction[68]

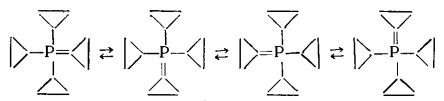


(CIX)

Next, the familiar transylidation process takes place.

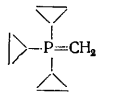
The application of ^{1}H NMR spectroscopic methods made it possible to discover many analogous instances of the degenerate tautomerism of ylides. Thus one may quote as an

example tricyclopropylcyclopropylidenephosphorane (CX) [69]:



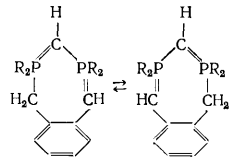
(CX)

It is of interest that the replacement of one cyclopropyl substituent by the methyl group immediately fixes the structure (CXI), as the more favourable, and proton migration ceases:



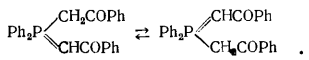
(CXI)

We may mention also the pentad system of type (CXII) [70]:



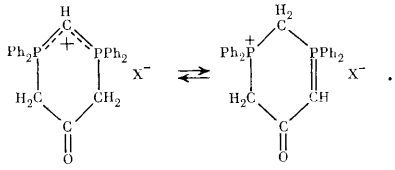
(CXII)

The introduction of strongly electron-accepting substituents into the methylene and methyl groups of trimethylmethylenephosphorane significantly reduces the barrier to tautomerisation. Thus the merging of the signals of the methylidyne and methylene groups in system (CXIII) takes place in $CDCl_3$ at −40°– −50 °C, while for a solution in SO_2 the merging takes place at −20 °C [71]:



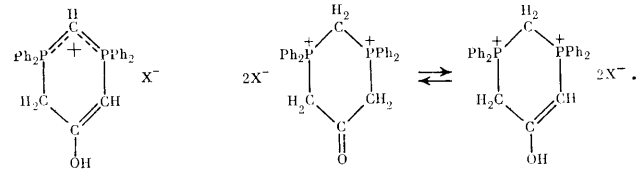
(CXIII)

The number of known cases of non-degenerate tautomerism in the triad $CH-\overset{|}{P}=C$ is much smaller. The first example of this kind was the tautomerism of 3,3,5,5-tetraphenyl-3,5-diphosphacyclohexenone, (CXIV) ⇌ (CXV), investigated by the authors of this review and their co-workers[72,73]:



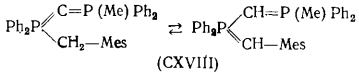
(CXIV) (CXV)

According to infrared spectroscopic data, the substance in the crystalline state has the structure (CXV): the infrared spectrum of a mull in hexachlorobutadiene shows bands at 1540–1550, 1345, and 880 cm^{-1} associated with the ν_1, ν_2, and ν_3 vibrations of the acylphosphinomethylene system, while OH bands are absent; according to NMR and infrared spectra, a solution in $CHCl_3$ contains simultaneously also the (CXIV) form (again at a low relative concentration). It is of interest that the enol form (CXVI) is not detected in the equilibrium mixture at all, while in the saturated system (CXVII) there is a distinct keto-enol equilibrium according to ^1H NMR and infrared spectroscopic data[74]:



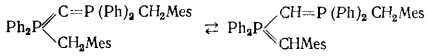
(CXVI) (CXVII)

Interesting examples of the non-degenerate tautomerism (CXVIII), (CXIX), and (CXX) in the $C=\overset{|}{P}-CH$ triad have been described recently[75]:



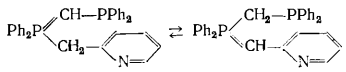
(CXVIII)

(3 : 1 ratio of different forms);



(CXIX)

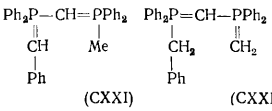
(3 : 2 ratio of different forms);



(CXX)

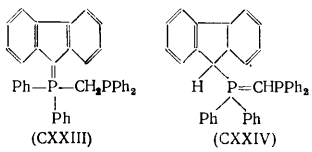
(3 : 1) ratio of different forms).

In the degenerate carbon–phosphorus–carbon tautomerism the forms involved are identical, their acidities are equal, and their contents in the equilibrium mixture are the same. For certain small differences between the structures of the forms, which are reflected in their relative CH acidities, a non-degenerate tautomerism is observed where the less acid form naturally predominates in the equilibrium mixture. On the other hand, if the structural differences become more significant, then the difference between the CH acidities increases and the equilibrium is almost completely displaced to one side. Thus the derivative (CXXI) is not tautomeric; it has the structure (CXXI) and not (CXXII):



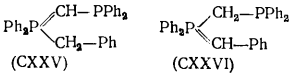
(CXXI) (CXXII)

The fluorenylidene derivative is also non-tautomeric, having the structure (CXXIII) and not (CXXIV):



(CXXIII) (CXXIV)

If the α-pyridyl substituent in system (CXX) is replaced by the phenyl substituent, which has a lower acidifying capacity, then the equilibrium is fully displaced towards the (CXXV) form and tautomerism with the (CXXVI) form is not manifested:



(CXXV) (CXXVI)

Such a sharp response of the position of the carbon–phosphorus–carbon tautomeric equilibrium to seemingly small changes in the character of the substituents at the CH groups can be explained by the very high slopes of the linear

correlations between the pK_a for the different forms and $\sum\sigma_{CH}^-$. Indeed the values of ρ in the expressions for the pK_a for non-tautomeric CH acids ($pK_a = pK_a^0 - \rho\sum\sigma_C^-$) vary from 10 to 25 as a function of the solvent, the counterion, etc.[46]

Small changes in $\sum\sigma_C^-$ induce large changes in the pK_a for the different forms. The difference between them ($\Delta pK_a = pK_1 - pK_2$) can then increase markedly, whereupon the position of the tautomeric equilibrium ($pK_T = \Delta pK_a$) is sharply altered.

IV. CONCLUSION

Not so long ago there was no information about the existence of PH ylides, P(OH) ylides, P(SH) ylides, etc. Studies in the 1970's led to the discovery of this new extensive field of organophosphorus chemistry. In this review we were concerned only with problems of the tautomerism of such ylides with the corresponding derivatives of tervalent phosphorus or phosphoryl, thiophosphoryl, etc. compounds. The prototropic migrations could be reliably treated in this instance from the standpoint of the theory of the tautomeric acid–base protolytic equilibrium. This is naturally extremely important. At the same time, it is essential to note that the proton transitions constitute only a part of the extensive chemistry of the new systems. There exists yet another very interesting field of dual reactivity of the corresponding ambident species, which can be negatively charged like the usual anions, but the corresponding neutral species are also possible if the initial protonated forms carry a positive charge. We were naturally unable to deal with this extremely interesting field of the chemical properties of new phosphorus ylides. There is a possibility also of other interesting and important reactions, for example, rearrangements, decomposition reactions, etc. Their elucidation has not so far proceeded very far, although interesting results have already been obtained. However, this is a subject for another article.

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The Arbuzov Rearrangement with Participation of Halogenoacetylenes as a Method of Synthesis of Ethynylphosphonates and other Organophosphorus Compounds

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The Arbuzov rearrangement with participation of halogenoacetylenes is examined and its possible application in the synthesis of a wide variety of hitherto inaccessible organophosphorus compounds is discussed.
The bibliography includes 50 references.

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I. INTRODUCTION

The Arbuzov rearrangement, discovered at the beginning of the century, has served for decades as one of the principal methods of synthesis of compounds with a phosphorus–carbon bond and has been an important method for the investigation of substances capable of nucleophilic substitution and addition reactions. Studies carried out in the Department of Organic Chemistry of the Lensovet Leningrad Technological Institute showed in 1962 that halogenoacetylenes with the halogen attached to the triple bond can be used successfully in this reaction[1]. The discovery of the Arbuzov rearrangement involving halogenoacetylenes not only revealed a new pathway to the synthesis of a wide variety of acetylenic phosphonates and other organophosphorus compounds based on them but also attracted attention to the study of the reactivities of halogenoacetylenes in relation to nucleophiles.

Although many halogenoacetylenes have long been known and convenient preparative methods for the synthesis of a series of compounds of this type have been proposed, for a long time they did not find applications in organic synthesis. At the beginning of the 1960s only a few reactions involving the nucleophilic substitution of the halogen in halogenoacetylenes were known[2] and on the whole it was assumed that their reactivity in relation to nucleophiles is low. It was postulated that, as in hypohalites, the halogen in halogenoacetylenes is "positive" and that this should promote oxidation-reduction processes and not nucleophilic substitution with elimination of the halogen as an anion. In reality, it was found that, at least in those cases where the second carbon of the halogenoacetylenes is linked to a group containing a multiple bond, to an aromatic ring, or to a heteroatom, the nucleophilic substitution of the halogen—the Arbuzov rearrangement leading to the formation of "normal" products (ethynylphosphonates and halogenoalkanes)—takes place readily and with a high yield[3-7]:

$$R{-}C{\equiv}C{-}X + P(OAlk)_3 \longrightarrow R{-}C{\equiv}C{-}P(O)(OAlk)_2 + AlkX \quad (X=Cl, Br)$$

During the past two decades, various investigators achieved the syntheses of a wide variety of ethynylphosphonates, including those hitherto inaccessible, studied the reaction mechanism, and demonstrated the possibility of employing the compounds obtained for the synthesis of various organophosphorus products based on them.

II. SYNTHESIS OF ACETYLENIC PHOSPHONATES

Among halogenoacetylenic compounds, bromoethynyl- and chloroethynyl-benzenes[1,2], conjugated bromoalkenynes[3,6], and bromoalkadiynes (1-bromopenta-1,3-diyne and 1-bromohexa-1,3-diyne)[4] were made to undergo the reaction successfully. Alkylhalogenoacetylenes are much less reactive and react only on heating, forming mixtures of products which are difficult to separate[5]. Nevertheless, when 1-bromo-oct-1-yne reacts with triethyl phosphite, the corresponding phosphonate is formed in a yield up to 20%; however, the authors showed that the reaction of 1-bromoalkynes with sodium dialkyl phosphites, which takes place at a reduced temperature (−70 °C) in tetrahydrofuran with a yield up to 75%,[7] constitutes a more suitable method of synthesis of alkylethynylphosphonates.

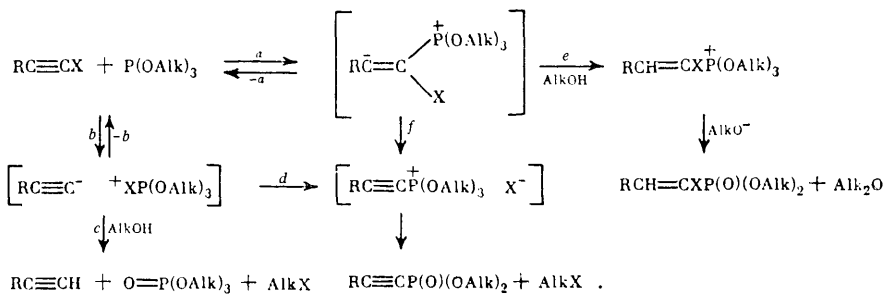
The rearrangement of trialkyl phosphites by halogenoacetylenes, containing a group with a metal belonging to the Fourth Period as the second substituent, has been achieved successfully. This not only permitted the synthesis of exotic dihetero-substituted acetylenes but also led to the discovery of a simple method of synthesis of unsubstituted ethynylphosphonate, which is otherwise difficult to obtain, and also of bromoethynyl phosphonate[9,10]:

$$Alk_3M{-}C{\equiv}C{-}X + P(OAlk)_3 \rightarrow Alk_3M{-}C{\equiv}C{-}P(O)(OAlk)_2 \rightarrow \begin{cases} \xrightarrow{\text{hydrolysis}} HC{\equiv}CP(O)(OAlk)_2 \\ \xrightarrow[(M=Sn)]{Br_2} BrC{\equiv}CP(O)(OAlk)_2 \end{cases} ; \quad M=Sn, Si$$

The rearrangement involving dichloro- and dibromo-acetylenes is especially interesting. Depending on the ratio of the dihalogenoacetylene and the phosphite, one or both halogen atoms can be substituted[5,11,12]:

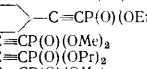
$$X{-}C{\equiv}C{-}X \xrightarrow{P(OAlk)_3} X{-}C{\equiv}C{-}P(O)(OAlk)_2 \rightarrow \xrightarrow{P(OAlk)_3} (AlkO)_2P(O)C{\equiv}CP(O)(OAlk)_2 .$$

This reaction has been used to synthesise symmetrical and mixed phosphonates[13]. The employment of this method for the synthesis of ethynylphosphine dioxides, which are of interest as dienophiles, has been reported[14]. In the presence of an excess of dihalogenoacetylene, highly reactive halogenoethynylphosphonates were obtained—they are convenient intermediates in the synthesis of previously inaccessible substituted ethynylphosphonates and derivatives of phosphonoacetic acid.



Ethynylphosphonates obtained by the Arbuzov rearrangement with participation of halogenoacetylenes, which were not indicated in a previous review[8], are listed in Table 1.

Table 1. Ethynylphosphonates obtained by the Arbuzov rearrangement from halogenoacetylenes*.

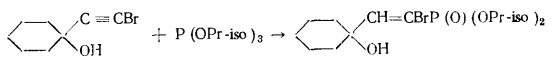
Compound	Yield, %	B.p., °C (*p*, mmHg)	*t*, °C	n_D^t, °C	d_4^t
$C_6H_{13}C{\equiv}CP(O)(OEt)_2$	15—20	128 (0.4)	20	1.4470	—
$CH_2{=}C(Et)C{\equiv}CP(O)(OMe)_2$	53	82 (0.15)	24	1.4818	1.127
$CH_2{=}C(Et)C{\equiv}CP(O)(OEt)_2$	60	82 (0.1)	25	1.4702	1.042
cis- $MeCH{=}C(Me)C{\equiv}CP(O)(OMe)_2$	52	90—95 (0.2)	23	1.5093	1.196
trans- $MeCH{=}C(Me)C{\equiv}CP(O)(OMe)_2$	30	81 (0.1)	24	1.4855	1.100
cis- $MeCH{=}C(Me)C{\equiv}CP(O)(OEt)_2$	52	102 (0.2)	20	1.4810	1.069
trans- $MeCH{=}C(Me)C{\equiv}CP(O)(OEt)_2$	57	86 (0.1)	23	1.4753	1.043
	77	147 (0.05)	23	1.5030	1.106
$ClC{\equiv}CP(O)(OMe)_2$	87	55 (2)	25	1.4569	—
$ClC{\equiv}CP(O)(OPr)_2$	84	98—99 (1)	20	1.4566	1.0978
$BrC{\equiv}CP(O)(OMe)_2$	62	89—91 (1)	20	1.4711	1.6308
$Me_3SiC{\equiv}CP(O)(OMe)_2$	70	60 (0.8)	20	1.4305	—
$Me_3SiC{\equiv}CP(O)(OEt)_2$	82	60—61 (0.01)	25	1.4437	—
$Et_3SnC{\equiv}CP(O)(OEt)_2$	82	150—151 (1)	20	1.4899	1.2797
$(MeO)_2P(O)C{\equiv}CP(O)(OMe)_2$	72	155—156 (1.5)	20	1.4473	—

Remarks. The table does not include compounds listed in the review of Ionin et al.[8] and a number of compounds quoted without an indication of the constants. A patent has been taken out[49] for a method of synthesis of the previously unknown[8] tetraethyl acetylenediphosphonate.

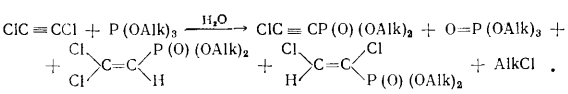
1. The Mechanism of the Rearrangement

Since the interaction of halogenoacetylenes with trialkyl phosphites is analogous to the usual rearrangement with participation of halogenoalkanes as regards the character of the rearrangement and the structure of the products, in this instance too one can put forward the usual mechanism of the rearrangement with the intermediate formation of a quasi-phosphonium compound[3]. Subsequent kinetic studies[15] confirmed the two-stage character of the rearrangement. The reaction is of second order (of first order with respect to each reactant). $\Delta H^{\neq} = 17-18$ kcal mol^{-1}, $-\Delta S^{\neq} = 26-29$ e.u. and the Hammett reaction constant $\rho \cong 2$ have been obtained for a series of chloro- and bromo-ethynylarenes p-$XC_6H_4C{\equiv}CY$ (X, Y = Cl, Cl; Cl, Br; H, Br; Me, Cl; Me, Br; MeO, Cl). The high negative activation entropy indicates the formation of a pair of ions in the rate-determining stage, which corresponds to a quasi-phosphonium mechanism of the rearrangement; the high value of ρ is an indication of the proximity of the reaction centre to the aryl group, which may correspond to attack by the nucleophile on the carbon atom nearest to the halogen (direction *a* in the scheme presented below). However, studies using a proton donor as a trap for the intermediate carbanions made it possible to specify the first stage in greater detail and to discover two possible directions of attack by the nucleophile—on the C(1) carbon atom and on the halogen atom X.[12,15,16]

Direction *b* has been confirmed by the formation of free acetylene (reduction, reaction *c*). Since the kinetic characteristics of the processes occurring when the reaction is carried out in the presence of alcohol change only slightly, the addition of a proton donor does not alter the mechanism radically. The occurrence of the reaction via pathway *e* has been confirmed experimentally in the interaction of tri-isopropyl phosphite with 1-bromoethynylcyclohexanol[16]:



and the study of the interaction of dichloroacetylene with trialkyl phosphites, which in the presence of moisture takes place partly with formation of dihalogenovinylphosphonate[12,17]:



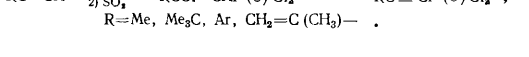
Thus the rearrangement proceeds via two competing pathways—with attack by the nucleophile on the C(1) atom and on the halogen atom.

The reactions of halogenoacetylenes with tertiary phosphines take place analogously but stop at the stage of the quaternary phosphonium salt[18—21].

2. Other Methods of Synthesis of Acetylenic Compounds With a Phosphorus-Containing Group At the Triple Bond

In order to assess the significance of the Arbuzov rearrangement as a method of synthesis of phosphonoacetylenic compounds, we shall consider other methods of synthesis of these substances[22,23]. The traditional method of synthesis of hetero-substituted acetylenes, namely the reaction involving metal acetylides, has been used mainly for the synthesis of compounds with a tricoordinate phosphorus atom and also for the preparation of unsubstituted ethynylphosphonate, which is difficult to obtain[8]. In the synthesis of higher derivatives, this method is relatively unsuitable owing to the difficulty of isolating the products.

The addition of phosphorus pentachloride to acetylenic hydrocarbons with subsequent dehydrochlorination is convenient for the synthesis of ethynylphosphonates but is restricted to a narrow range of compounds[24—26]:



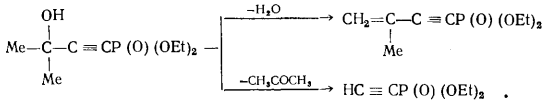
This method is inapplicable to higher alkylacetylenes, since it leads to phosphonates with multiple bonds remote from the phosphorus atom.

Phosphorus-containing propadiene derivatives readily undergo prototropic isomerisation with migration of the double bond to the phosphorus-containing group[27,28]. This property can be used for the synthesis of 1-propynylphosphonates and the analogous phosphine oxides in a single stage via the acetylene–allene–acetylene isomerisation of propargyl phosphites or propargyl phosphinites[29]:

$$(AlkO)_2POCH_2C\equiv CH \rightarrow CH_2=C=CHP(O)(OAlk)_2 \rightarrow MeC\equiv CP(O)(OAlk)_2 .$$

The reaction involving higher acetylenic phosphonates stops at the allene stage and prototropic isomerisation under the influence of bases leads to a mixture of compounds in which isomers with a triple bond remote from the phosphorus atom predominate[28].

The formation of certain acetylenic phosphonates by the reaction of halogenoacetylenes with sodium dialkyl phosphites was mentioned above. The phosphonoacetylenic alcohols obtained by this method were converted into other derivatives—halides, enynylphosphonates, and unsubstituted ethynylphosphonate[6]:



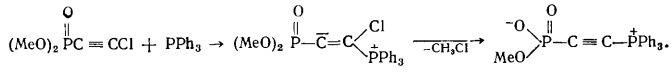
The formation of acetylenic phosphines by the reaction of phosphides with halogenoacetylenes is known[30]. The synthesis of a series of compounds with a phosphorus(III) atom at the triple bond has been reported: primary and tertiary phosphines, phosphinite esters, and *N,N*-dialkylphosphinamidates[31–33].

A number of acetylenic phosphonates have been obtained as a result of subsequent reactions of halogenoethynylphosphonates formed when dihalogenoacetylenes and trialkyl phosphites react. These reactions will be considered in the next section.

III. REACTIONS OF HALOGENOETHYNYLPHOSPHONATES

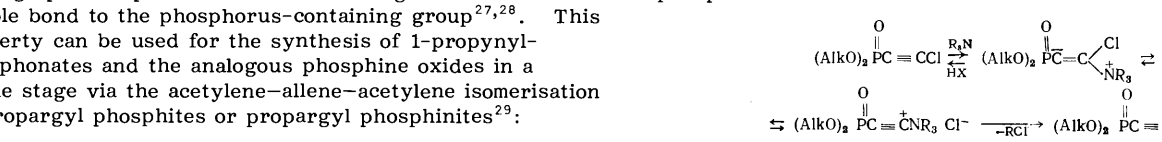
1. Reactions with Retention of the Triple Bond

Chloro- and bromo-ethynylphosphonates, obtained by the reaction of dihalogenoacetylenes with tertiary phosphites, contain a halogen atom at the triple bond activated by the electron-accepting dialkyl phosphonate group. These compounds are capable of nucleophilic substitution of the halogen with retention of the triple bond, which makes it possible to synthesise a wide variety of ethynylphosphonic acid derivatives hitherto inaccessible. The possibility of involving these compounds in the Arbuzov rearrangement with formation of ethylidynediphosphonates was mentioned above. The interaction of chloroethynylphosphonate with triphenylphosphine leads to the formation of a quaternary phosphonium salt, but the resulting chloride anion attacks another electrophilic centre (the phosphonate group), which leads to the formation of a dipolar ion[19]:



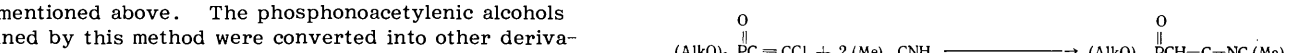
Chloroethynylphosphonates react vigorously with tertiary aliphatic amines forming ynammonium salts. In the case of triethylamine such a salt is unstable and decomposes with formation of an ynamine on slight heating[34].

The ynammonium salt obtained from trimethylamine is more stable and the formation of the ynamine requires heating to 150–160 °C. On treatment with proton donors, the salt decomposes with liberation of the initial chloroethynylphosphonate[17,35]:



Ynamines are formed readily also on interaction of chloroethynylphosphonates with secondary amines, but in this case a second mole of the amine combines with the hydrogen chloride evolved[35].

The reaction with a sterically hindered primary amine (t-butylamine) proceeds analogously, but the proton migrates in the product with formation of a keten imine structure[36]:



The reaction with ammonia involves the prototropic shift of two hydrogen atoms and the triple bond migrates to the nitrogen atom with formation of phosphonoacetonitrile[5].

Stronger nucleophiles (alkoxide anions) attack the chloroethynylphosphonate at the phosphono-group, which leads to the rupture of the P–C bond and the formation of phosphates. However, on treatment with the phenoxide anion, it is possible to achieve the substitution of the halogen with formation of phenoxyethynylphosphonates[17]:

$$(AlkO)_2P(O)C\equiv CCl \xrightarrow{PhO^-} (AlkO)_2P(O)C\equiv COPh + Cl^- .$$

Treatment of chloroethynylphosphonate with an equivalent amount of sodium ethanethiolate leads to the substitution of the halogen by the ethylthio-group[17]:

$$(AlkO)_2P(O)C\equiv CCl + EtS^- \rightarrow (AlkO)_2P(O)C\equiv CSEt + Cl^- .$$

Neither reaction goes to completion and in the presence of an excess of the nucleophile they are accompanied by the addition of the latter with formation of ethylenic compounds and phosphonoacetic acid derivatives.

Chloroethynylphosphonate is reactive toward organomagnesium compounds, which makes it possible to obtain alkylethynylphosphonates[5]:

$$(AlkO)_2P(O)C\equiv CCl + EtMgBr \rightarrow (AlkO)_2P(O)C\equiv CEt .$$

The constants of the new compounds with a phosphorus-containing group at the triple bond are listed in Table 2.

2. Reactions Involving the Triple Bond

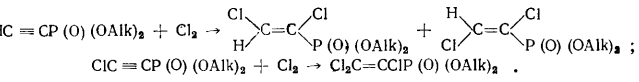
Ethynylphosphonates contain the highly reactive triple bond, which permits their use in the synthesis of a wide variety of organophosphorus compounds.

Catalytic hydrogenation of ethynylphosphonates at a palladium catalyst is stereospecific and *cis*-1-alkenylphosphonates are formed following the addition of one mole of hydrogen[25,37]:



cis-Ethylenediphosphonate[*cis*-$(EtO)_2P(O)CH=CHP(O).(OEt)_2$] has been obtained by hydrogenating acetylenediphosphonate.

Chlorination of ethynylphosphonate leads to the formation of a mixture of *cis*- and *trans*-addition products. The third (geminal) dichlorovinylphosphonate is formed in the Arbuzov rearrangement of dichloroacetylene and trialkyl phosphites in the presence of moisture (see Section II). Chlorination of chloroethynylphosphonate leads to the formation of a trichloroethylene derivative[12]:



Bromination results in a mixture of isomeric 1,2-dibromo-2-chlorovinylphosphonates[17].

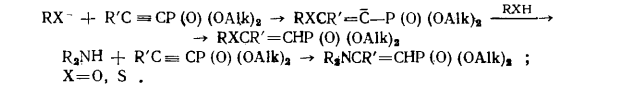
Table 2. Ethynylphosphonates obtained by different methods (other than the Arbuzov rearrangement)*.

Compound	Yield, %	B.p., °C (*p*, mmHg))	n_D^{20}	d_4^{20}
By the interaction of halogenoacetylenes with sodium dialkyl phosphites (Ref.7)				
MeC≡CP(O)(OEt)$_2$	37	84—87 (0.3)	1.4450	
EtC≡CP(O)(OEt)$_2$	40	100 (0.4)	1.4437 (23°)	
PrC≡CP(O)(OEt)$_2$	75	110 (0.4)	1.4463 (22°)	
BuC≡CP(O)(OEt)$_2$	70	115 (0.6)	1.4478 (24°)	
BuC≡CP(O)(OBu)$_2$	72	143 (0.5)	1.4503 (19°)	
AmC≡CP(O)(OEt)$_2$	72	125 (0.4)	1.4481 (22°)	
HexC≡CP(O)(OEt)$_2$	69	128 (0.4)	1.4470 (22°)	
HOCH$_2$C≡CP(O)(OEt)$_2$	18	160 (0.3)	1.4570	
HOCH(Me)C≡CP(O)(OEt)$_2$	60	162 (0.4)	1.4556 (21°)	
HOC(Me$_2$)C≡CP(O)(OEt)$_2$	68	133 (0.4)	1.4500 (25°)	
From carbinols, by the substitution of the hydroxy-group by halogen and dehydration (Ref.7)				
CH$_2$=C(Me)C≡CP(O)(OEt)$_2$	65	107 (0.5)	1.4630 (24°)	
CH$_2$CHClC≡CP(O)(OEt)$_2$	55	123 (1)	1.4586	
From 2-chloroalka-1,3-dienylphosphonates, by dehydrochlorination (Ref.26)				
CH$_2$=C(Me)C=CP(O)Cl$_2$	95	41—42 (0.05)	1.5165	1.2885
Me$_2$C=C(Me)C≡CP(O)Cl$_2$	67	70—71 (0.1)	1.5279	1.2210
MeCH=C(Me)C≡CP(O)Cl$_2$	70	47—48 (0.05)	1.5189	1.2379
By the substitution of chlorine in chloroethynylphosphonates (see Section III. 1)				
EtSC≡CP(O)(OEt)$_2$	48	132 (1)	1.1750	1.4909
Me$_2$NC≡CP(O)(OMe)$_2$	87	124 (1)	1.1970	1.4789
Me$_2$NC≡CP(O)(OEt)$_2$	84	129 (1)	1.1166	1.4741
Me$_2$NC≡CP(O)(OPr)$_2$	82	153 (1)	1.0385	1.4729
Et$_2$NC≡CP(O)(OMe)$_2$	84	131 (1)	1.1780	1.4763
Et$_2$NC≡CP(O)(OEt)$_2$	44	145—147 (1)	1.4680	1.0538
Et$_2$NC≡CP(O)(OPr)$_2$	79	168 (1)	1.4689	1.0245

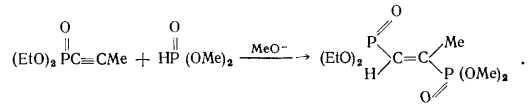
Note. The table does not include compounds quoted without an indication of their physicochemical constants.

The addition of hydrogen halides to phosphine oxide with a triple bond takes place with difficulty, which can be explained by the protonation of the phosphoryl oxygen. On the other hand, hydrochlorination of chloroethynylphosphonate takes place fairly readily and leads to the formation of a geminal dichloride[12,17].

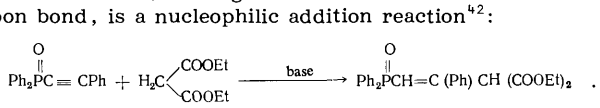
Ethynylphosphonates show a particular tendency to undergo nucleophilic addition reactions involving the triple bond. Alkoxide and thiolate anions as well as secondary amines attack the triple bond at the C(2) atom with formation of the corresponding 2-hetero-substituted vinylphosphonates[38-40]:



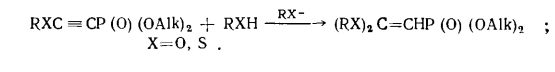
Dimethyl phosphite adds to the 1-propynylphosphonic ester with formation of the *E*-isomer of 1,2-propylenediphosphonate[41]:



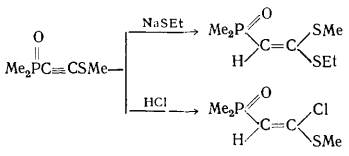
The condensation of diphenyl(phenylethynyl) phosphine with malonic ester, leading to the formation of a new carbon–carbon bond, is a nucleophilic addition reaction[42]:



Alkoxy- and alkylthio-ethynylphosphonates combine with a nucleophile at the C(2) atom with formation of 2,2-dihetero-substituted vinylphosphonates[17]:

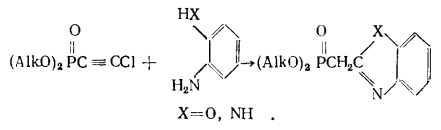


It has been shown[43] that the addition of a mercaptan and hydrogen chloride to dimethyl(methylthioethynyl)phosphine oxide proceeds in the same manner:

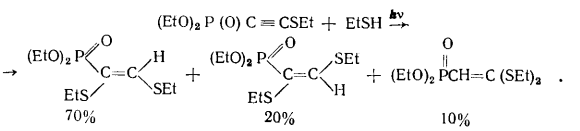


Hydration of hetero-substituted ethynylphosphonates results in the formation of phosphonoacetic acid derivatives.

Treatment of halogenoethynylphosphonates with an excess of a nucleophile results in the substitution of the halogen and the addition of the nucleophile to the triple bond. Bifunctional nucleophiles lead to the formation of heterocyclic compounds[44,45]:

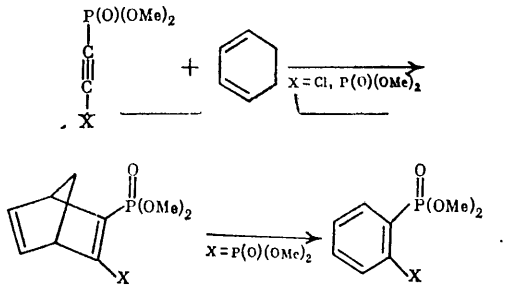


The interaction of ethylthioethynylphosphonate with ethanethiol in the absence of a basic catalyst and under the influence of ultraviolet light leads to the formation of a mixture of isomeric compounds in which 1,2-di(ethylthio)-vinylphosphonates predominate, which indicates a free-radical reaction mechanism[12]:

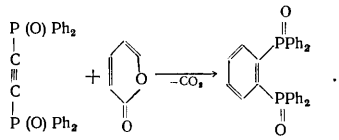


Ethynylphosphonates are reactive in diene synthesis and 1,3-dipolar cycloaddition reactions. Dimethyl chloroethynylphosphonate and tetramethyl acetylenediphosphonate interact with cyclohexa-1,3-diene to form norbornadiene

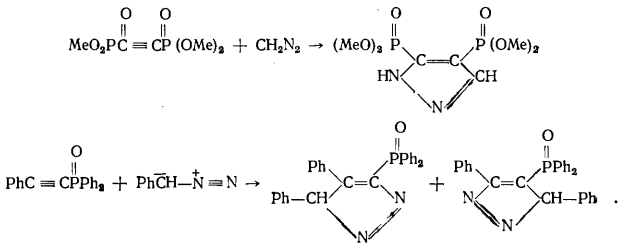
derivatives; in the second case the reaction can be completed by the formation of *o*-bis(dimethylphosphono)-benzene[11]:



The reaction of bis(diphenylphosphinyl)acetylene dioxide with dihydropyran-2-one leads to an analogous result[14]:



Diazoalkanes add to ethylidyne diphosphonate and diphenyl(phenylethynyl)phosphine oxide[14,16]. The second reaction proceeds non-regiospecifically:

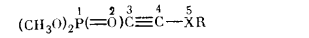


Pudovik, Khusainova, and co-workers investigated a series of reactions involving 1,3-dipolar addition to ethynylphosphonates, established the regiospecificity of the reaction and the dipolar activity of the triple bond as a function of the substituents at the phosphorus atom, and analysed the reaction mechanism within the framework of the molecular orbital perturbation theory. These and other studies of dipolar addition to ethynylphosphonates have been described in a review[47].

Thus ethynylphosphonates undergo all typical reactions characteristic of compounds with an activated triple bond.

IV. THE ELECTRONIC STRUCTURE AND PHYSICAL CHARACTERISTICS OF ETHYNYLPHOSPHONATES

Quantum-chemical calculations in terms of the CNDO/2 approximation indicate the following distribution of effective charges in model ethynylphosphonates[17]:



XR	1	2	3	4	5
H	0.469	−0.256	−0.141	0.010	0.060
Cl	0.450	−0.221	−0.135	0.088	−0.047
SCH_3	0.439	−0.224	−0.127	0.020	−0.018

In the infrared spectra of ethynylphosphonates, the $\nu(C\equiv C) = 2175-2180\ cm^{-1}$ stretching vibration band corresponds to the triple bond and there is an absorption band due to the P=O group at 1240–1270 cm^{-1}. The ^{31}P NMR spectra of ethynylphosphonates show that the phosphorus atom attached to the triple bond resonates in the region of a strong field (from −8 to 10 p.p.m. in alkyl-, chloro-, bromo-, and alkylthio-ethynylphosphonates), undergoing slight downfield displacement in the presence of electron-donating substituents at the triple bond (−3.5 to −3.7 p.p.m. in alkoxyethynylphosphonates and −2.8 to −2.2 p.p.m. in dialkylaminoethynylphosphonates). In ethylnylphosphine oxides the resonance of the ^{31}P nuclei is observed in the range +7 to +9 p.p.m. (relative to 85% H_3PO_4).

The chemical shifts of the acetylenic carbon atoms in the ^{31}C NMR spectra of ethynylphosphonates vary with the substituents at the phosphorus and C(2) carbon atoms. These signals can be readily identified because of the significant difference between the $J_{^{13}C}$ and $J_{^{31}P}$ constants. 2-Hetero-substituted ethynylphosphonates are characterised by the following ^{13}C NMR parameters[12,17]:

Compound	$\delta_{C(1)}$	$\delta_{C(2)}$	$J_{C(1)-P}$	J (—P)
$(CH_3O)_2P(O)C{\equiv}CBr$	54.04	75.88	302.4	56.6
$(EtO)_2P(O)C{\equiv}CCl$	57.49	74.56	300.3	56.7
$(MeO)_2P(O)C{\equiv}CCl$	66.71	62.15	296.7	52.0
$(EtO)_2P(O)C{\equiv}CSEt$	82.40	90.00	284.0	71.3
$(PrO)_2P(O)C{\equiv}CNMe_2$	48.01	63.89	320.2	39.1

Ethynylphosphonates are characterised by considerable electrical dipole moments. Analysis based on an additive scheme indicates the polarisation of the system, which induces the appearance of an additional contribution of 0.7–1.0 D directed towards the phosphorus-containing group[48,50].

Halogenoacetylenes with a halogen atom at the triple bond and particularly those containing unsaturated or aromatic groups or a heteroatom as the second substituent in the ethynyl group undergo the Arbuzov rearrangement with formation of ethynylphosphonates. This reaction constitutes the most general method of synthesis of a wide variety of hitherto inaccessible highly unsaturated phosphorus compounds. The rearrangement involving dihalogeneoacetylenes, which leads, depending on the conditions, to the formation of acetylenediphosphonates or halogenoethynylphosphonates, is of special interest. The latter phosphonates are capable of participating in halogen substitution reactions with retention of the triple bond.

The reactions of ethynylphosphonates with participation of the triple bond make it possible to synthesise a wide variety of unsaturated and saturated functional derivatives of organophosphorus compounds.

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Molecular Rearrangements Accompanied by the Migration of Phosphoryl Groups between Two nucleophilic Centres

A.N.Pudovik and M.G.Zimin

The review surveys instances of the reversible and irreversible migration of phosphoryl groups $\left(\geq P{=}O,\ \geq P{=}S,\ \geq P{=}N{-}\right)$ between two heteroatoms (N, O, S, and Se); this type of rearrangement is characterised by retention of the coordination number of the phosphorus atom. The rearrangements of phosphorylated aminoalcohols, mercaptoalcohols, oximes, and the products of the addition of partially esterified acids of tetracoordinate phosphorus to cyano-compounds, carbodiimides, and keten imines, proceeding via a stage involving the formation of unstable phosphoranes are considered. Much attention is devoted to tautomeric processes in which the phosphoryl, thiophosphoryl, and iminophosphoryl groups are the migrating moieties.
The bibliography includes 109 references.

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I. INTRODUCTION

There has been a considerable development in recent years of the study of rearrangements accompanied by the migration of phosphoryl and other groups with a tetracoordinate phosphorus atom, whose driving force is the deficiency of electron density at the phosphorus atom. In an isomerisation process, the deficiency of electron density at the phosphorus atom in the final or intermediate product diminishes.

The study of rearrangements of this type makes it possible to discover the causes and factors promoting the stabilisation or rupture of bonds in the P–S–C, P–N–C, P–O–C, etc. groups present in derivatives of tetracoordinate phosphorus acids and throws light on the characteristics of the mechanism of nucleophilic substitution at the tetrahedral phosphorus atom. The phosphorylation and phosphoryl group transfer reactions are responsible for many vitally important biochemical processes.

The aim of the present review was to examine and (wherever possible) to treat systematically studies devoted to rearrangements involving the migration of phosphoryl groups between two nucleophilic centres in which the coordination number of the phosphorus atom remains ultimately unaltered. Attention is devoted also to the preparative aspect, since the migration of phosphoryl groups is observed in the synthesis of many organophosphorus compounds and also in the preparation of biologically active phosphoric acid derivatives.

In view of the wide variety and novelty of the rearrangements considered, their mechanisms have been inadequately investigated and the schemes put forward are tentative and open to discussion. The most characteristic migrations of phosphoryl and thiophosphoryl groups are of the 1,3- and 1,4-types, which can occur via both intramolecular and intermolecular mechanisms depending on the nature of the nucleophilic centre and the migrating moiety. Sometimes the 1,3-migration is accompanied by the elimination of the phosphorus-containing group.

The 1,2-migrations of phosphoryl groups between two heteroatoms occur in tetracoordinate phosphorus derivatives (I) with P–P bonds and are always accompanied by a decrease of the coordination number of one of the phosphorus atoms; such reactions have been largely surveyed in earlier publications[1,2]:

$$RR^1P(X)-PRR^1(Y) \rightleftarrows RR^1P(Y)-X-PRR^1(Y)\ ;$$

(I)

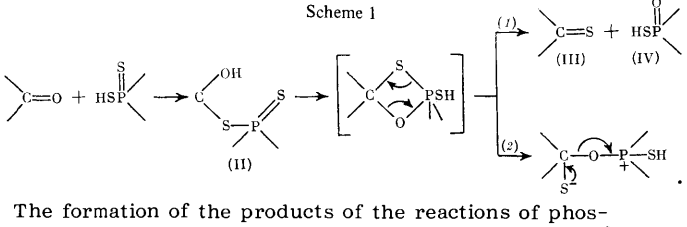
X, Y=O, S; R, R¹=Alk, AlkO, Ar, ArO, Alk_2N .

The isomerisation of symmetrical pyrophosphorothioates to asymmetric compounds[3] and of *S*-phosphorylthiocyanates to *N*-phosphorylisothiocyanates [4] has also been described in detail in the literature and is not therefore discussed here.

II. THE 1,3-S → O MIGRATIONS

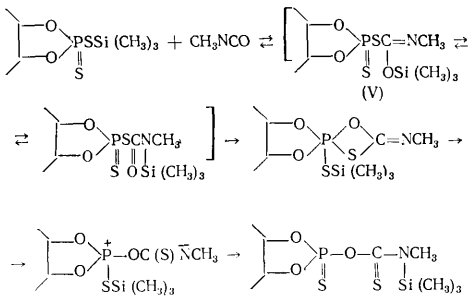
There are few examples of such migrations. The transformation of unstable *gem*-monothioketals (1-hydroxylalkyl phosphorodithioates) (II) into thiocarbonyl compounds (III) and tetracoordinate phosphorus thioacids can be regarded formally as the 1,3-O → S migration of the thiophosphoryl groups[5] (Scheme 1). A one-stage mechanism (pathway *1*) and not a two-stage mechanism (pathway *2*) is then postulated with formation of a transition state analogous to that in the Wittig reaction[6]:

Scheme 1



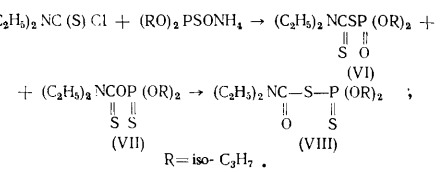
The formation of the products of the reactions of phosphorodithioic acid with aromatic aldehydes and ketones[6], carbostyril[7], carboxylic acid esters and amides[8,9], isocyanates[10,11], and triphenylphosphine oxide[11] and of *O,O*-dialkyl S-trimethylsilyl phosphorodithioates with benzaldehyde and acetophenone[12] has been described in terms of this or an analogous scheme. There are no data confirming the mechanism of these reactions which are referred to as the "*O,S*-exchange reactions".

A rearrangement of compounds (V) in which the 1,3-S → O shift is not accompanied by the elimination of the phosphorus-containing fragment, and it is therefore possible to assume that it proceeds via a number of stages, has been reported recently[13]:



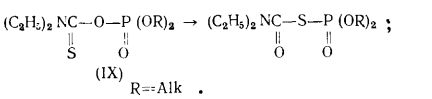
A thiophosphoryl group with acyclic substituents migrates in this situation to the nitrogen and not the oxygen atom[13].

When *N*,*N*-diethylthiocarbamoyl chloride reacts with ammonium di-isopropyl phosphorothioate in acetone, a mixture of *N*-acylation and *O*-acylation products [compounds (VI) and (VII)] is formed in proportions of 4 : 1; the *O*-acylation products (VII) predominate in dimethylformamide (in proportions of 3 : 1):[14]



On heating and vacuum distillation, the mixed anhydride (VII) rearranges to the carbamate (VIII).[14]

An analogous rearrangement of compounds (IX) with migration of the phosphoryl group takes place much more readily than in the synthetic process:

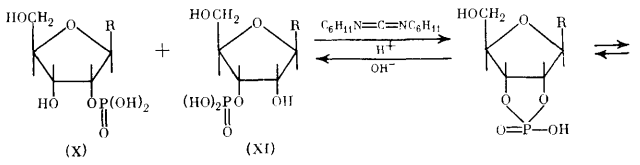


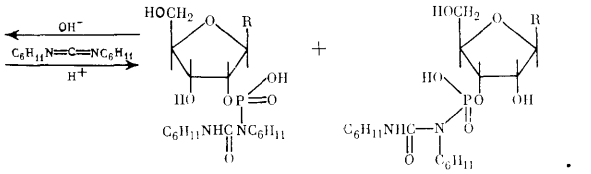
It has been shown that these rearrangements are irreversible both at room temperature and on heating.

III. REARRANGEMENTS OF IMIDOYL DERIVATIVES OF PHOSPHORIC AND PHOSPHOROTHIOIC ACIDS

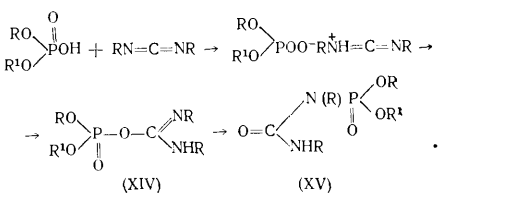
The first reports of the 1,3-O → N migration of phosphoryl groups in imidoyl phosphates were associated with the development of the carbodiimide phosphorylation method, which has found extensive applications in the synthesis of biologically important phosphate esters[15,16]. *N*-Phosphorylated ureas (XII) and (XIII) were identified among the products of the reaction of phosphoric acid monoesters (X) and (XI) with dicyclohexylcarbodiimide (Scheme 2):[17]

Scheme 2

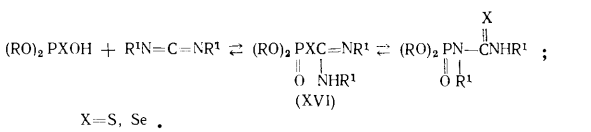




Subsequently the formation of *N*-phosphorylated ureas in the carbodiimide phosphorylation method was frequently confirmed[18–22]. In all cases the initial formation of the intermediates (XIV), which rearrange to the ureas (XV), was postulated. The "imidoyls" (XIV) have been recently isolated[23]:



The rearrangements of analogous S- or Se-phosphorylated isothio- or isoselenoureas have been reported in a study of the reactions of dialkyl phosphorothioates, phosphoroselenoates, and phosphorodithioates with carbodiimides[24]. Dialkyl phosphorothioates and phosphoroselenoates add to the C=NH group via the sulphur or selenium atom respectively:



The addition products (XVI) can be detected by ^{31}P NMR.[25] Their rearrangement is reversible[24]; under the usual conditions, the equilibrium is almost wholly displaced to the right. In the reactions of dicyclohexylcarbodiimide with sterically hindered dialkyl phosphorodithioates the intermediate has been isolated in the form of a salt (XVII) with HBF_4,[23] while in the reactions with the corresponding dialkyl phosphates this cannot be done. According to X-ray diffraction data, the distance between the nitrogen and phosphorus atoms in the molecule of compound (XVII) is 3.49 Å. For the oxygen analogue with the same bond angle, the distance between the nitrogen and phosphorus atoms has been estimated as 2.34 Å, which is equal to the sum of the van der Waals radii of the nitrogen and phosphorus atoms; according to the authors[23], this is the cause of the faster rearrangement of *O*-phosphorylisoureas.

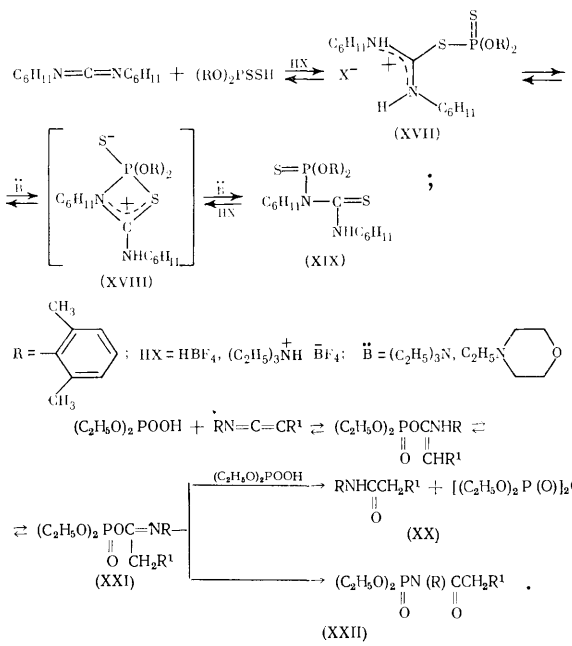
The rearrangement of *S*-thiophosphorylisothioureas (XVII) and the reverse rearrangement are controlled by the acidity of the medium[26]. Bases and acids promote the S → N and N → S migrations respectively. The rearrangement of compounds (XVII) and (XIX) proceeds via the intermediate (XVIII); the transformation (XIX) → (XVII) proceeds via the protonation of the nitrogen in the P–N bond (Scheme 3). The acid-catalysed transformations of compounds (XVII) and (XIX) into the initial compounds show that the reaction system is in overall equilibrium.

A kinetic study of the rearrangement of compounds containing the C–S–P fragment to *N*-phosphorylthioureas showed[26] that the reaction is of first order and takes place without the formation of other kinetically significant intermediates.

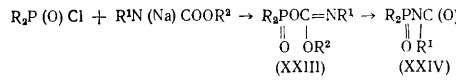
The study of the stereochemistry of the transformation of S(Se)-phosphorylisothio(seleno)ureas into *N*-phosphorylthio-(seleno)ureas [27] demonstrated the complete retention of the configuration at the phosphorus atom. The data obtained support an intramolecular isomerisation mechanism.

The products of the reactions of diethylphosphoric acid with keten imines[28] are, together with tetraethyl pyrophosphate and the amide (XX), the *N*-phosphorylated amides (XXII), formed as a result of the rearrangement of the *O*-phosphorylated derivatives (XXI).

Scheme 3



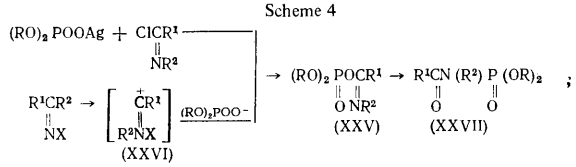
The kinetically controlled products of the phosphorylation of the sodium derivatives of alkyl carbamates are the imidoyl phosphates (XXIII), which were detected in the reaction mixture by infrared spectroscopy[29]:



Compounds (XXIII) readily isomerise to the *N*-phosphorylated carbamates (XXIV).

The high phosphorylating capacity of imidoyl phosphates stimulated investigators to develop convenient methods for their synthesis. The imidoyl phosphates (XXV) have been synthesised (in accordance with Scheme 4) by the reaction of iminochlorides with the silver salts of dialkylphosphoric acids and by a method involving the Beckmann rearrangement[30]. They have not been isolated in a pure form.

Scheme 4

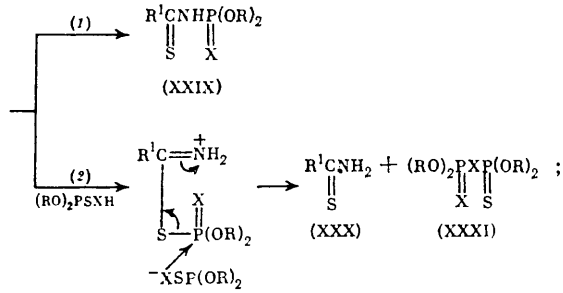


Their formation has been demonstrated by hydrolytic and aminolytic reactions. It has been noted that, when the substituent R^2 in compounds (XXV) is a methyl group, then isomerisation to compounds (XXVII) takes place readily, whereas in the case where R^2 is a secondary alkyl or phenyl group, there is no appreciable migration of the dibenzylphosphoryl group[31]. According to the data of Zieman et al.[32], the products of the reactions of the alkali metal or ammonium salts of dialkylphosphoric acids with iminochlorides are *N*-phosphorylated amides. The high stability of the imidoyl phosphates (XXV), formed as a result of the thermal Beckmann rearrangement from *O*-phosphorylated derivatives of acetophenone oxime is, therefore, incomprehensible[30].

The O → N migration of the phosphoryl groups in imidoyl phosphates is due to the considerable energy gain on formation of the amide structure, the energy of formation difference $E_{amide} - E_{imidoyl}$ being capable of reaching 20 to 25 kcal mol^{-1} and for this reason the rearrangements are usually irreversible. However, the transformation of *N*-phosphorylamides into *O*-phosphorylisoamides has been observed in the gas phase by mass spectrometry[33]. The analogous 1,3-S → N migrations of phosphoryl groups are reversible. The isomerisation of *N*-phosphorylthioamides has been observed mass-spectrometrically[34]. Such reversibility can also be illustrated in relation to the rearrangement of the products of the addition of partially esterified tetracoordinate thio-acids to cyano-compounds.

The reactions of tetracoordinate phosphorus thioacids with cyano-compounds have attracted the attention of investigators as a method of synthesis of thioamides[35]. In recent years they have been investigated from the standpoint of the rearrangements of imidoyl phosphorothioates. The products of the interaction of tetracoordinate phosphorus dialkylthio- and dialkyldithio-acids with nitriles[36-39], iminoesters[40,41], thiocyanates[42,43], phenyl cyanate[44], and cyanamides[45] isomerise. It has been shown in relation to a large number of examples that, in the first stage of these reactions, the phosphorus thio- and dithio-acids add to the cyano-group with formation of the imidoyl derivatives (XXVIII) (Scheme 5). Phosphoromonothioic acids attack the cyano-group via the sulphur atom[38,44]. However, these compounds are extremely unstable and isomerise even during the reaction to the corresponding *N*-phosphorylated thioamides, thio- and dithio-carbamates, and thioureas (XXIX) (pathway *1*). Compound (XXVIII) can be detected in certain cases by ^{31}P NMR.[37]

Scheme 5

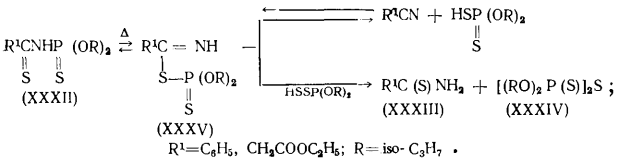


R^1=Alk, Ar, Alk_2N, AlkS, ArS, ArO, CCl_3, $CHCl_2$, $CH_2COOC_2H_5$; R=Alk .

The imidoyl phosphorothioates (XXVIII) also exhibit an exceptionally high phosphorylating capacity and are cleaved at the P–S bond already in the course of the reaction under the influence of the initial thio-acid (pathway *2*), which leads

to the formation of thioamides, thio- and dithio-carbamates, thioureas (XXX), and pyrophosphates (XXXI).

All these reactions are complex and a large number of a wide variety of products are formed. However, under certain conditions, the isomerised products can be isolated in high yields[36,43,46]:



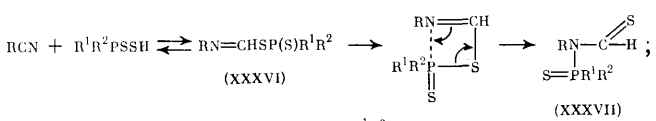
(XXXII) (XXXV) (XXXIII) (XXXIV)

$R^1=C_6H_5$, $CH_2COOC_2H_5$; R = iso-C_3H_7 .

On heating, there is a possibility also of the reverse N → S migration of the thiophosphoryl groups. Thus, when *N*-phosphorylated thiobenzamide or ethoxycarbonylthioacetamide (XXXII), obtained from phosphorous dithioacids and nitriles, were heated, the thioamides of the corresponding carboxylic acids (XXXIII) and pyrophosphorotrithioate were isolated[36]. Compounds (XXXII) are then converted into the imidoyl phosphates (XXXV) with a P–S–C linkage, which are in equilibrium with the initial dithioacids and nitriles, which is confirmed by the isolation of nitriles from the reaction mixture. The dithioacid formed as a result of the dissociation of compound (XXXV) cleaves the P–S bond in the imidoyl phosphorodithioate, as described above. This pathway is characteristic of all the reactions of tetracoordinate phosphorus thio- and dithioacids with cyano-compounds.

The products (XXXVI) of the α-addition of phosphorus dithioacids to 2,6-dimethyl- or 2,6-diethyl-phenylisonitrile (XXXVI) [47] isomerise to *N*-thiophosphorylthioformamides (XXXVII). The main products of the reactions of cyclohexyl-, phenyl-, 4-tolyl-, or 2,5-xylyl-isonitriles with phosphorus dithioacids (Scheme 6) are the formimidoyl phosphorodithioates (XXXVI).[48] In some cases they were isolated in a pure form.

Scheme 6



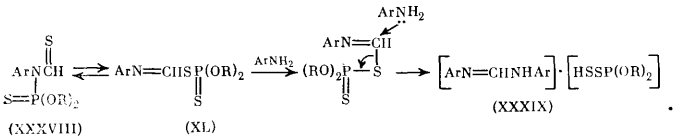
(XXXVI) (XXXVII)

R = C_6H_{11}, C_6H_5, 4-$CH_3C_6H_4$, 2,5-$(CH_3)_2C_6H_3$; R^1R^2 = AlkO .

Even at room temperature, compounds (XXXVI) gradually isomerise to the thioformamides (XXXVII). It has been found[47] that the rearrangement is a first-order reaction. On replacement of the ethoxy-substituents at the phosphorus atom by methoxy-substituents, the rate of rearrangement increases. The reaction is sharply retarded on passing from phosphorodithioates to phosphonodithioates; derivatives of diphenylphosphinodithioic acid are altogether incapable of the rearrangement[47,48]. The tendency towards isomerisation increases with increase of the nucleophilicity of the nitrogen[48,49]. These data suggested[49] that the rearrangement proceeds via an intramolecular four-centre mechanism involving nucleophilic substitution at the tetrahedral phosphorus atom. However, the intramolecular character of this rearrangement cannot be regarded as rigorously demonstrated.

It is believed[47] that this isomerisation is irreversible. According to other investigations[48,49], heating of *N*-dialkylthiophosphorylthioformamides (XXXVIII) with aromatic amines leads to the formation of the phosphorodithioate salts of *N,N'*-diarylformamidines (XXXIX) (Scheme 7) with considerable yields (70–80%).

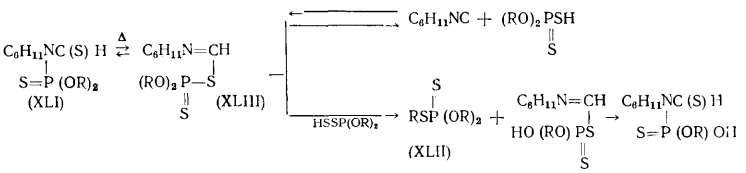
Scheme 7



(XXXVIII) (XL) (XXXIX)

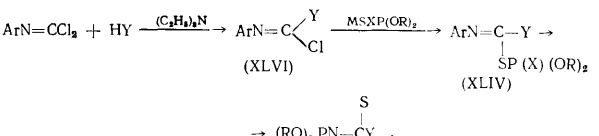
The formation of compound (XXXIX) can be explained only by postulating the reverse 1,3-N → S migration of the thiophosphoryl group, resulting in the formation of imidoyl phosphorodithioates (XL), which give rise to the salts (XXXIX) as a result of the attack by the amine on the imino-carbon atom. The direct interaction of compounds (XXXVIII) with amines results in the formation of other products[48,49].

O,O,S-Trialkyl phosphorodithioates (XLII) and cyclohexylisonitrile are obtained in high yields of pyrolysis *in vacuo* of *N*-dialkyl-*N*-cyclohexylthiophosphorylthioformamides (XLI), obtained by the reaction of phosphorus dithioacids with cyclohexylisonitrile[48]:



(XLI) (XLIII) (XLII)

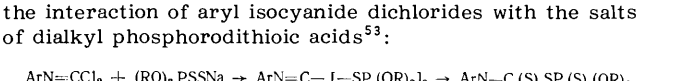
Evidently compounds (XLI) isomerise on heating to compounds (XLIII), which are in equilibrium with the initial isonitrile and the dithioacid. The dithioacid dealkylates[50] the ester group at the phosphorus atom, which results in the formation of the phosphorodithioates (XLII). According to Malz et al.[51], the stepwise substitution of the chlorine atoms in aryl isocyanide dichlorides initially by an alkoxy-, alkylthio-, or amino-group and then by the phosphorothioate or phosphorodithioate group results in the formation of stable compounds with the imidoyl structure of the type of (XLIV). It was later established[52] that in all cases the final products of these reactions are the products of the rearrangement of the imidoyl phosphates (XLIV), namely *N*-thiophosphorylated thio- and dithio-carbamates or the thioureas (XLV). It is noteworthy that, when salts of dialkylphosphoromonothioic acids are introduced into the reaction with the iminochlorides (XLVI), derivatives with the P=O group are formed:



(XLVI) (XLIV) (XLV)

X=O, S; M=H, Na, K, NH_4; R=C_3H_7, iso-C_3H_7; Y=OCH_3, iso-SC_3H_7, $N(C_2H_5)_2$.

The structure of *S,S*-bis(dialkylthiophosphoryl) isodithiocarbamates (XLVII) has been attributed to the products of the interaction of aryl isocyanide dichlorides with the salts of dialkyl phosphorodithioic acids[53]:

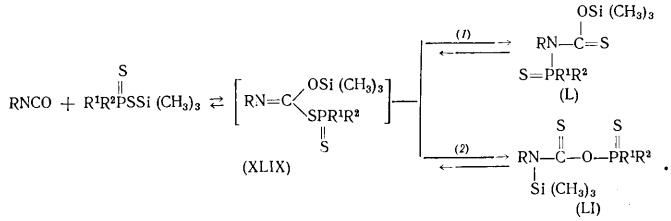


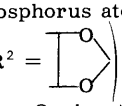
(XLVII) (XLVIII)

However, detailed studies have shown[54] that in this case compounds (XLVII) rearrange to *N*,*S*-bis(dialkylthiophosphoryl) dithiocarbamates (XLVIII). It is noteworthy that the isomerisation of compounds (XLIV) and (XLVII) takes place irreversibly even at 160 °C.

An interesting situation arises when two groups capable of migration are present in imidoyl phosphorothioates. When silyl phosphorodithioates react with isocyanates[13] (Scheme 8), the imidoyl phosphorodithioates (XLIX) are formed in the first stage. In the case of the acylic dialkoxy-derivatives ($R^1 = R^2 = OAlk$), the 1,3-S → N migration with formation of compound (L) is observed. The introduction of the phenyl or trichloroacyl substituent at the nitrogen atom hinders the S → N migration of the thiophosphoryl group, apparently owing to the reduction of the nucleophilicity of the nitrogen atom:

Scheme 8

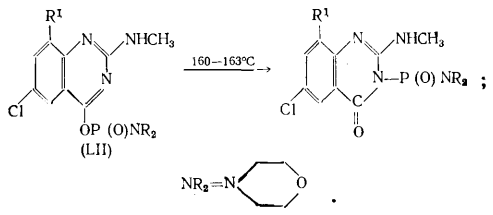


If the phosphorus atom is incorporated in a five-membered ring ($R^1R^2 =$ ), then compounds (XLIX) rearrange via the 1,3-S → O migration of the thiophosphoryl group to the *N*-silyl derivative (LI).

There are several reports in the literature of the 1,3-S → N or O → N migrations of the phosphoryl and thiophosphoryl groups in the series of heterocyclic compounds. The phosphorylation of the ambident anions of heterocyclic amides[55] by phosphorochloridates takes place both at the oxygen atom and at the nitrogen atom. *O*-Phosphorylation is the kinetically controlled reaction stage.

The stability of compounds of type (LII) (Scheme 9) compared with the acyclic imidoyl phosphates (XXV) and (XXI) is due to the presence of a conjugated system of multiple bonds:

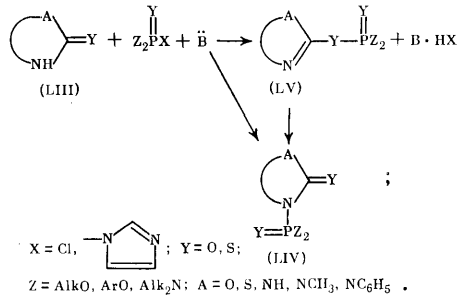
Scheme 9



The thermodynamically more favourable *N*-phosphorylated products are formed via the rearrangement of the *O*-derivatives, which has been demonstrated for compound (LII).

The phosphorylation of a series of heterocycles (LIII) containing urea, carbamate, thiourea, and dithiocarbamate fragments has been investigated (Scheme 10):[56]

Scheme 10

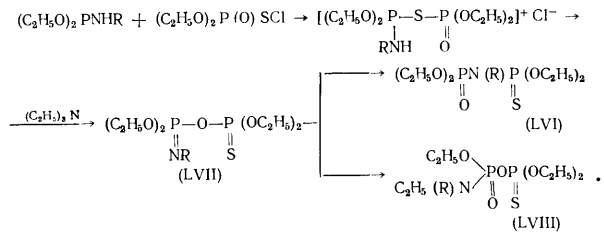


It was found that the phosphorylation is controlled by structural factors both in the substrate and in the reagent. In most cases *N*-phosphorylation products (LIV) are formed as a result of the isomerisation of the *O*- or *S*-phosphorylated intermediates (LV). In one instance the *S*-phosphorylation product (LV, A = Y = S, Z = OC_6H_5), which can be regarded as a model of "O-phosphobiotin", was isolated. However, this product does not rearrange. In the case of the oxygen analogues, evidence has been obtained for the existence of kinetically controlled *O*-phosphoryl derivatives on the basis of their ability to function as phorphoryl group transferring agents. The greater stability of the *S*-phosphorylation products compared with that of their oxygen analogues can be explained by the reduced electrophilicity of the phosphorus atom and the greater length of the P–S–C linkage compared with the P–O–C linkage, which hinders the intramolecular migration in the rigid cyclic molecule. Compounds with an open-chain structure, for example, phosphorylated isothioureas, readily isomerise[26,27] (see above).

Thus, in the 1,3-migration of phosphoryl and thiophosphoryl groups, there is a favourable situation in the N=C–O triad for an intramolecular reaction mechanism, while the question of the character of the migration in the N=C–S triad remains controversial; apparently these migrations proceed both intramolecularly and intermolecularly, depending on the structure, the experimental conditions, and the presence of catalysts.

Rearrangements accompanied by the 1,3-O → N migration of phosphoryl groups have been observed also in the iminophosphorus triad. After the reaction of phosphoramidites with phosphorylsulphene chloride[57,58], the phosphoramidite (LVI), formed via Scheme 11 as a result of the rearrangement of the phosphorimidate (LVII), was detected among the reaction products:

Scheme 11



Depending on the nature of the substituent at the nitrogen atom, compounds of type (LVII) are stabilised in two ways[58,59]. If R is an alkyl or phenyl group, the phosphorus-containing

substituent migrates with formation of compound (LVI). If R is an electron-accepting group, then the nucleophilicity of the nitrogen atom is reduced, which entails the migration of the ethyl substituent of the ethoxy-group with formation of compound (LVIII).

It has been found recently[60] that S → N migration takes place in the mixed anhydrides of phosphinimidic and phosphorodithioic acids (LIX):

$$(RO)_2P(S)-S-P(C_6H_5)_2 \rightarrow C_6H_5N(S)-P(OR)_2 ;$$
$$NC_6H_5 \qquad\qquad S=P(C_6H_5)_2$$
(LIX)

R=Alk .

The rearrangement proceeds irreversibly at room temperature.

IV. PHOSPHORYLOTROPIC TAUTOMERISM

The tautomeric processes in which the phosphoryl, iminophosphoryl, or thiophosphoryl groups are the migrating moieties (phosphorylotropism) were first observed for imidoyl derivatives of phosphorothioic acid[61].

A convenient method for the synthesis of compounds used in the study of phosphorylotropism may be provided by the reactions of isothiocyanates with sodium dialkyl phosphites involving the phosphonate–phosphorothioate rearrangement[49] of thiocarbamoylphosphonic acid derivatives in which the P–C bond is influenced by the neighbouring electron-accepting group. The characteristic features of this rearrangement have been investigated recently. It was found that the isomerisation of thiocarbamoylphosphonates requires the presence of electron-accepting substituents at the nitrogen atom[62] and the use of an equimolar or a nearly equimolar amount of a strong base in order to convert the thiocarbamoyl phosphonate into the ionised form active in the rearrangement.

The reactions of sodium di-isopropyl phosphite with methyl and allyl isothiocyanates in boiling benzene for 10–12 h lead to unisomerised products with a P–C bond[62]; the interaction of dialkyl phosphites and their analogues with isothiocyanates in the presence of catalytic amounts of bases under mild conditions has the same result[63–65].

The interaction of the sodium or potassium salts of dialkyl phosphites with phenyl isothiocyanate at 80–145 °C is accompanied by the phosphonate–phosphorothioate rearrangement of the phenylthiocarbamoylphosphonates (LX) to dialkyl *S*-phenyliminomethyl phosphorothioates and phosphorodithioates (LXI).[66] The products (LXI) are also formed on heating the pure phenylthiocarbamoylphosphonates (LX) in an equimolar amount of sodium dialkyl phosphite[66]:

$$C_6H_5NCS + HP(X)R_2 \rightarrow \underset{(LX)}{C_6H_5NHC(S)P(X)R_2} \xrightarrow{NaXPR_2}$$
$$\rightarrow \underset{(LXI)}{C_6H_5N{=}CH{-}S{-}P(X)R_2} \rightleftarrows C_6H_5NCH{=}S \quad ;$$
$$X{=}PR_2$$
(LXII)

X=O, S .

Compounds (LXI) are capable of phosphorylotropic tautomerism[62]. At room temperature the equilibrium is 90–95% displaced towards the thioformamide (LXII). However, like the compounds described by Zinin and co-workers[48,67], compounds (LXI) undergo further reactions on heating. The interaction of sodium di-isopropyl phosphite with phenyl isothiocyanate (Scheme 12), followed by treatment of the reaction mixture with methyl iodide, yielded a tautomeric mixture, from which compound (LXIII) and (LXIV) can be isolated[62]:

Scheme 12

$$C_6H_5NCS + (RO)_2PO^- \longrightarrow \underset{(LXV)}{C_6H_5N{-}C(S^-){-}P(OR)_2(O)} \longrightarrow$$

$$\xrightarrow{CH_3I} \underset{(LXIII)}{C_6H_5N{=}C(CH_3)SP(O)(OR)_2} \rightleftharpoons \underset{(LXIV)}{C_6H_5N(CH_3)C(S){-}P(O)(OR)_2} ;$$

R = iso-C_3H_7

It has been suggested[66,68] that the rearrangement of thiocarbamoylphosphonates proceeds via a three-centre $S_N2(P)$-mechanism. In the anion (LXV) there are two nucleophilic centres capable of attacking the electrophilic phosphorus atom. The nucleophilic reactivity of sulphur is apparently greater than that of nitrogen. This has also been demonstrated in relation to the reaction of *O,O*-di-isopropylthiophosphoryl isothiocyanate with sodium diethyl phosphite (Scheme 13):

Scheme 13

$$(RO)_2P(S)NCS + (C_2H_5O)_2PO^- \longrightarrow \underset{}{(RO)_2N{-}C(S^-){-}P(OC_2H_5)_2(O)} \longrightarrow$$

$$\xrightarrow{CH_3I,\ \Delta} \underset{(LXVI)}{(RO)_2PN{=}C(CH_3)SP(OC_2H_5)_2} ;$$

R = iso-C_3H_7 .

The 1,2-C → S migration product (LXVI) is then formed; compounds whose formation mechanism involves the 1,2-C → N migration of the diethylphosphoryl group were not detected. Separate experiments demonstrated that the presence of electron-accepting substituents at the imino-nitrogen atom in compounds of type (LXVI) prevents phosphorylotropic transformations. On the other hand, such transformations are characteristic of *N*-aryl-substituted compounds (LXVII), which can be obtained by the reaction of iminochlorides with salts of tetracoordinate phosphorus monothio- and dithioacids[61]:

$$RC(Cl){=}NC_6H_4Y + NaXSPR^1R^2 \rightarrow \underset{}{RC(SP(X)R^1R^2){=}NC_6H_4Y} \rightleftarrows \underset{(LXVIII)}{RC(S)N(C_6H_4Y){-}P(X)R^1R^2} ;$$
(LXVII)

X=O, S; Y=H, *p*-Br, *p*-CH_3, *p*-CH_3O, *p*-NO_2;
R=C_6H_5; R^1=R^2=AlkO .

The salts of tetracoordinate phosphorus monothio-acids always react via the sulphur atom of the thiophosphoryl group.

The occurrence of the phosphorylotropism of compounds of type (LXIII) and (LXVII) has been demonstrated by a combined infrared, ^1H NMR, and ^{31}P NMR spectroscopic study. Two signals in the ranges 58–64 and 78–85 p.p.m. (for the phosphorodithioate derivatives) or −3–−5 and 15–18 p.p.m. (for the phosphoromonothioate derivatives), referring to the thioamide (LXVIII) and imidothiolic (LXVII) forms respectively, are observed in the ^{31}P spectra at room temperature. On heating, the intensity of the indicator signal of the imidothiolic form (LXVII) increases, while that of the thioamide form (LXVIII) falls. When the initial temperature is restored, the system returns to the original state.

In certain cases the tautomers can be isolated in a pure form under the usual conditions. Thus the thioamide isomer is usually crystallised from solutions in pentane.

With increase of temperature, an increase of the content of the thermodynamically less favourable imidothiolic form (a) is observed in all cases (Table 1). Table 1 shows that the conversion of the isomer (A) into the isomer (B) is exothermic. The quantity ΔH does not change in the temperature range 19–120 °C.

Table 1. The influence of temperature on the thermodynamic characteristics of the tautomeric equilibrium (condensed phase) [54]*

$C_6H_5C{=}NC_6H_4Y\text{-}p \rightleftarrows C_6H_5C(S{-}P(X)(OR)_2){-}NC_6H_4Y\text{-}p$

(A) (B)

R	X	Y	$-\Delta H$, kcal mol^{-1}	292 K a, %	292 K $-T\Delta S$, kcal mol^{-1}	373 K a, %	373 K $-T\Delta S$, kcal mol^{-1}
CH_3	S	H	1.3	42	1.1	52	1.4
C_2H_5	S	H	2.6	45	2.3	66	3.1
C_3H_7	S	H	3.4	44	3.2	76	4.4
iso-C_3H_7	S	H	3.4	51	3.4	83	4.5
C_4H_9	S	H	5.0	48	4.7	82	6.3
iso-C_3H_7	S	CH_3	2.9	47	2.6	64	3.5
iso-C_3H_7	S	Br	2.2	73	2.6	83	3.5
iso-C_3H_7	O	Br	4.0	11	1.3	25	1.7
C_2H_5	O	H	2.7	5	1.0	12	1.3

*Here and henceforth a represents the content of the isomer (A).

The free energies ΔG do not exceed 2 kcal mol^{-1},[54] which falls within the range of tautomeric processes on the thermodynamic scale[69]. The quantities ΔH and $T\Delta S$ are comparable, from which it follows that the state of equilibrium is influenced not only by the difference between the heats of formation but also by the difference between the entropies. At room temperature the enthalpy factor predominates somewhat over the entropy factor, but, with increase of temperature, the entropy factor begins to play a major role and becomes dominant for imidoyl phosphorodithioates at 100 °C.

The observed relation reflects the influence of two opposed thermodynamic factors. As a consequence of the large barrier to the "amide rotation",[70] the transition to the thioamide entails the loss of degrees of freedom by the molecule and an increase of the absolute value of the entropy, which destabilises the thioamide. On the other hand, the large energy gain on formation of the P–N and C=S bonds stabilises the thioamide form.

Compounds with the P=O group are influenced by temperature to a lesser extent than their thio-analogues (Table 1). The enthalpy factor for these compounds predominates somewhat even at 100 °C; comparison of the ΔG shows that the replacement of the P=S group by P=O leads to an increase of the difference between the thermodynamic stabilities of the tautomers.

The composition of the tautomeric mixtures depends on the state of aggregation. In the crystalline state the imidothiolic isomer (A) is not usually detected by infrared spectroscopy. In the liquid phase at the same temperature the content of the isomer (A) is considerable.

The composition of the tautomeric mixture in solutions differs strongly from its composition in the liquid or crystalline state. Since the two forms belong to different classes of organic compounds, the influence of the nature of the solvent is significant. Transition to solutions affects the thermodynamic characteristics of the phosphorylotropic tautomerism in different ways and can entail a shift of equilibrium in the opposite direction. The equilibrium position in both the condensed phase and in solutions is influenced by the enthalpy and entropy factors.

The results of the study of the dependence of K_{TS} on the nature of the solvent (Table 2) were treated by the method described in Palm's book[71]. The regression equation is

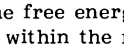
$$\lg K_{TS} = 0.196 + (0.915 \pm 0.114)Y + (0.657 \pm 0.207)P + (0.124 \pm 0.017)\cdot 10^{-2} B \quad (r = 0.986),$$

where P is the polarisability, Y the polarity, and B the nucleophilicity of the solvent. The contribution of the electrophilicity of the solvent is insignificant. Thus the position of the tautomeric equilibrium is greatly influenced not only by electrostatic interactions but also by specific interactions.

Table 2. The influence of the nature of the solvent on the position of the equilibrium (c = 0.1 M, 292 K) [54]

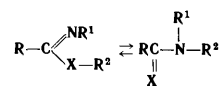
$C_6H_5C{=}NC_6H_4OCH_3\text{-}p \rightleftarrows C_6H_5C(S{-}P(S)(OC_3H_7\text{-iso})_2){-}NC_6H_4OCH_3\text{-}p$

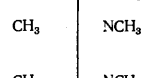
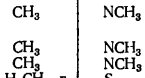
(A) (B)

Solvent	a, %	K_{TS}	$-\Delta G$, kcal mol^{-1}
—*	19	4.26	0.81
CCl_4	36	1.78	0.33
CS_2	33	2.03	0.41
$C_6H_5CH_3$	33	2.03	0.41
C_6H_6	31	2.23	0.46
$CHCl_3$	31	2.23	0.46
	29	2.45	0.52
CH_2Cl_2	27	2.70	0.58
$C_6H_5NO_2$	26	2.85	0.61
C_6H_5Br	26	2.85	0.61
C_6H_5I	25	3.00	0.64
C_6H_5Cl	24	3.17	0.67
$C_6H_4(CH_3)_2\text{-}p$	31	2.23	0.46
C_6H_5CN	23	3.35	0.70
$BrCF_2{-}CF_2Br$	22	3.55	0.73
CH_3CN	18	4.56	0.84
$C_6H_5C(O)CH_3$	16	5.25	0.96
$(CH_3)_2C{=}O$	14	6.14	1.05

*Condensed phase.

Table 3. The activation paramters for the tautomeric transformation [54,73]

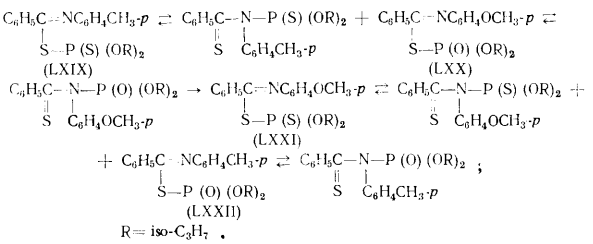


Compound	R	R^1	X	R^2	$\Delta G^{\neq}$, kcal mol^{-1}
(LXXIII)	C_6H_5	CH_3	NCH_3	$O{=}P(OC_2H_5)_2$	24.9 (447 K)
(LXXIV) *	C_6H_5	CH_3	NCH_3	$C_6H_5N{=}P(OC_2H_5)_2$	23.6 (447 K)
(LXXV) **	C_6H_5	CH_3	NCH_3	$O{=}P(OCH_2CF_2CHF_2)_2$	18.8 (350 K)
(LXXVI)	C_6H_5	CH_3	NCH_3		⩽8 (173 K)
(LXXVII)	CF_3	CH_3	NCH_3		21.7 (447 K)
(LXXVIII)	C_6H_5	CH_3	NCH_3	$P(O)F_2$	⩽8
(LXXIX)	$CHCl_2$	CH_3	NCH_3	$O{=}P(OC_2H_5)_2$	>25
(LXXX)	C_6H_5	$C_6H_4CH_3\text{-}p$	S	$P(S)(OC_3H_7\text{-iso})_2$	21.2 (398 K)
(LXXXI) ***	C_6H_5	$C_6H_4OCH_3\text{-}p$	S	$P(S)(OC_3H_7\text{-iso})_2$	20.0 (388 K)

*$\Delta H^{\neq}$ = 18.1 kcal mol^{-1}, $\Delta S^{\neq}$ = −12.4 e.u.
**$\Delta H^{\neq}$ = 9.4 kcal mol^{-1}, $\Delta S^{\neq}$ = −27 e.u.
***$\Delta H^{\neq}$ = 17.1 kcal mol^{-1}, $\Delta S^{\neq}$ = −8.1 e.u.

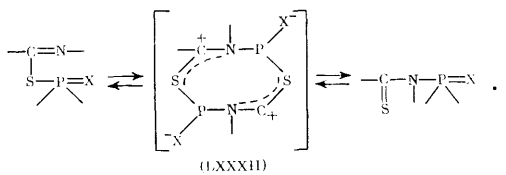
The barrier to the *E*, *Z*-topomerisation of the imidoyl form is evidently low (~10 kcal mol^{-1}) and the individual tautomers are not detected by ^{1}H NMR in the temperature range 30 to 100 °C. The barriers to the "amide" rotation about the P–N bond in N-di-isopropylphosphorylthioacetanilide and *N*-di-isopropylphosphorylthiopropionanilide are 14.8 and 14.6 kcal mol^{-1} respectively[70]. The phosphorylotropism in the thioamide triad is the slowest dynamic process (ΔG = 20–21 kcal mol^{-1}) (Table 3).

It has been noted that the rate of equilibration for *N*-thiophosphorylthioamides depends on the concentration of the solution, which indicates the intermolecular character of the tautomerism. This is confirmed by the identity of the ^{1}H NMR spectra of compounds (LXIX) and (LXX) and the artificial mixture of the tautomers (LXIX)–(LXXII) prepared taking into account the intermolecular exchange:



EPR and ^{31}P NMR studies using the method of chemically induced nuclear polarisation have made it possible to exclude the radical mechanism of phosphorylotropism. It has been suggested[54] that the phosphoryl exchange involving the imidoyl derivatives of tetracoordinate phosphorus proceeds via the cyclic dimeric form (LXXXII) and constitutes a kind of transacylation reaction involving the transfer of the reaction centre (Scheme 14):

Scheme 14

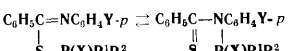


(LXXXII)

The dependence of the tendency towards tautomerism on structural factors is consistent with the proposed mechanism. The introduction at the carbon atom of the C=N double bond in imidoyl phosphorothioates and imidoyl phosphorodithioates of substituents which promote the delocalisation of the positive charge on the carbon atom of the intermediate (LXXXII) facilitates the tautomeric transformations. This is manifested by the fact that the replacement of the phenyl group by the methyl group or by a hydrogen atom leads to the absence of tautomerism. In this case imidoyl phosphorodithioates (LXVII) readily isomerise at room temperature to the corresponding thioamides (LXVIII),[48,54] but the reverse transformation is observed only on heating. When the phenyl group is replaced by the t-butyl group, the imidoyl isomer is the only one present and is incapable of rearrangement.

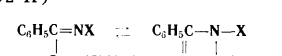
The environment of the phosphorus atom influences radically the position of the tautomeric equilibrium (Table 4). With increase of the length of the alkoxy-group, the equilibrium is displaced somewhat towards the imidoyl isomer, while on replacement of the P=S by the P=O group, there is a sharp shift in the direction of the thioamide isomer. The replacement of one alkoxy-group at the phosphorus atom by an alkyl or phenyl substituent in compounds with both P=O and P=S groups results in the attainment of equilibrium only at 180–200 °C. It has been demonstrated by differential thermal analysis that the process proceeds via a single stage, which is not inconsistent with the proposed mechanism. When both alkoxy-groups are replaced by phenyl groups, the rearrangement of imidoyl phosphinodithioates does not take place either at room or elevated temperatures. The products of the postulated isomerisation (*N*-phosphinothioylthioamides), obtained by other methods[72], are incapable of the reverse rearrangement with the 1,3-N → S migration of the diphenylphosphinothioyl group. An increase of the barrier to the interconversion in this instance is evidently associated with the decrease of the electrophilicity of the phosphorus atom and steric hindrance. In particular, the ligand exchange in the intermediate (LXXXII) is hindered by the weaker apicophilic properties of the alkyl and phenyl groups compared with the alkoxy-groups[74].

Table 4. The influence of the nature of the substituent at the phosphorus atom on the tautomeric transformation (292 K) [54]



R^1	R^2	X	Y	*a*, %	
				0.3 M solution in CCl_4	Condensed phase
CH_3O	CH_3O	S	H	—	42
C_2H_5O	C_2H_5O	S	H	45	45
C_3H_7O	C_3H_7O	S	H	47	44
iso-C_3H_7O	iso-C_3H_7O	S	H	57	51
C_4H_9O	C_4H_9O	S	H	58	48
iso-C_3H_7O	iso-C_3H_7O	O	H	—	5
iso-C_3H_7O	iso-C_3H_7O	S	NO_2	100	100
iso-C_3H_7O	iso-C_3H_7O	O	NO_2	—	40
iso-C_3H_7O	C_2H_5	S	H	100	100
iso-C_3H_7O	C_2H_5	S	CH_3	100	100
C_6H_5	C_2H_5	S	H	100	100
C_6H_5	C_6H_5	O	H	100	100

Table 5. The influence of the substituents at the nitrogen atom on the position of the tautomeric equilibrium (condensed phase, 292 K) [54]

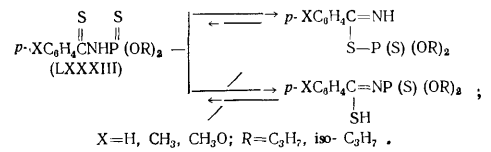


R	X	*a*, %	R	X	*a*, %
C_2H_5	$C_6H_4OCH_3$-*p*	19	C_2H_5	C_6H_4Br-*p*	65
C_2H_5	$C_6H_4OCH_3$-*o*	20	iso-C_3H_7	$C_6H_4NO_2$-*p*	100
C_2H_5	$C_6H_4CH_3$-*p*	35	iso-C_3H_7	CH_3	0
C_2H_5	C_6H_5	45	iso-C_3H_7	H	0

The introduction of electron-accepting substituents into the benzene ring at the nitrogen atom shifts the equilibrium towards the imidoyl isomer (Table 5). Electron-donating substituents displace the equilibrium in the opposite direction. When the aryl group is replaced by a methyl group or a hydrogen atom, the thioamide isomer is the only one present. For compound (LXXXIII), equilibrium, strongly displaced in the direction of the thioamide isomer, is

observed at elevated temperatures[75]. Thus substituents capable of delocalising the positive charge on the nitrogen atom of the intermediate (LXXXII) promote the tautomeric transformations.

It has been shown for compounds (LXXXIII) [75] that, when the capacities for the 1,3-migration of hydrogen and the phosphoryl group are identical, phosphorylotropic and not thione–thiol tautomerism obtains:



X=H, CH_3, CH_3O; R=C_3H_7, iso-C_3H_7 .

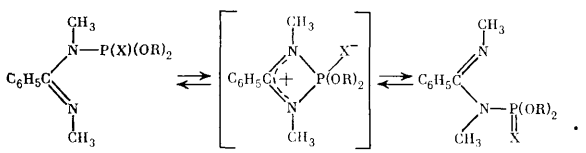
The study of the chemical behaviour of tautomeric *N*-phosphorylthioamides revealed their phosphorylating capacity and a high tendency to undergo reactions of the type of transacylation. When a mixture of the tautomers (LXXXV) and (LXXXVI) in benzene, where the contents of the imidoyl and amide forms are approximately the same, was treated with aromatic amines, the phosphorodithioate salts of arylamidines (LXXXVII) were isolated (Scheme 15). The tautomers (LXXXV) and (LXXXVI) hydrolyse to the thioamides (LXXXVIII), disproportionate with formation of the pyrophosphate (LXXXIX) and the sulphide (XC), and react with heavy metal ions to form complexes with the isoamide structure (XCI).[75,76] The products of the reaction of the tautomers (LXXXV) and (LXXXVI) with carboxylic acids are the amides (XCII) and the acyl phosphorothioates and phosphorodithioates (XCIII) (thioacetic acid reacts analogously).

The formation of the benzamides (XCII) and the phosphorothionates (XCIII) shows that the reactions with acids proceed via a mechanism involving transacylation as the first stage; this can be demonstrated by ^{31}P NMR and by isolating the product of the addition of di-isopropylphosphorodithioic acid to acrylonitrile when the reaction with acetic acid is carried out in the presence of the latter. These results suggest that the dissociative mechanism of the tautomeric transformation is unlikely. If the P=S bond were dissociated, one would expect the formation of thiobenzanilide and dialkyl phosphite, which, however, have not been isolated or detected by physicochemical methods.

Thus not only the thioamide but also the imidoyl form possesses dual reactivity involving both electrophilic centres—the phosphorus atom and the carbon atom of the C=N bond.

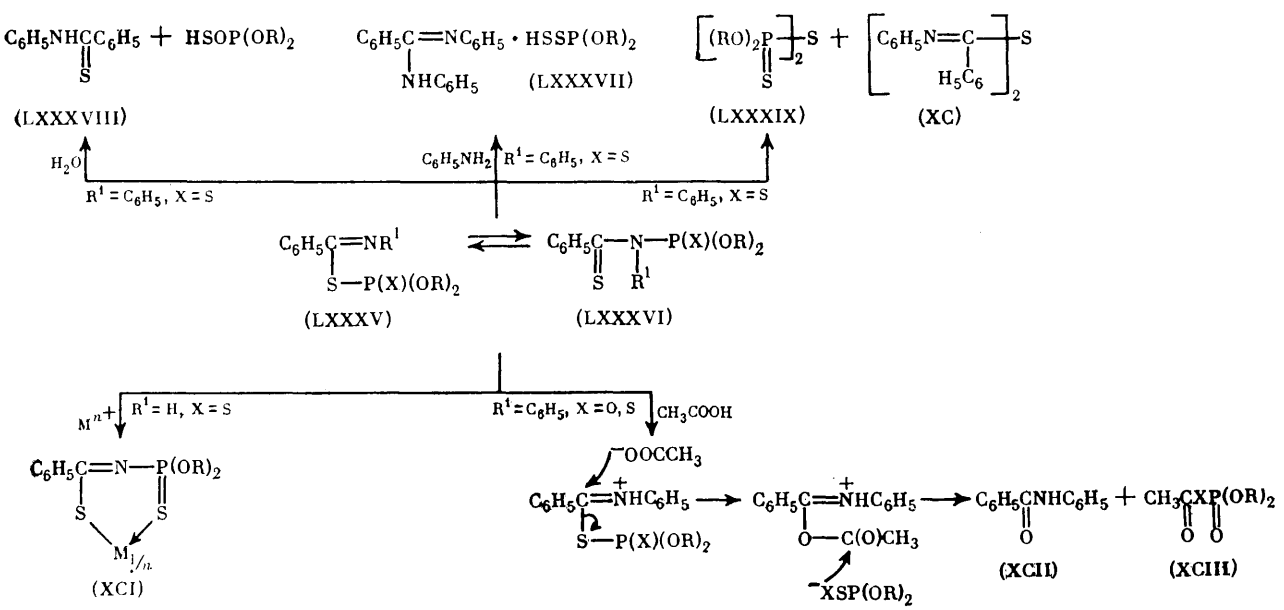
After the discovery of phosphorylotropism in the thioamide triad, the stereochemical behaviour of the phosphorylated *N*,*N'*-dimethylbenzamidines was explained by the occurrence of tautomeric transformations (Scheme 16):[77]

Scheme 16



(XCIV)

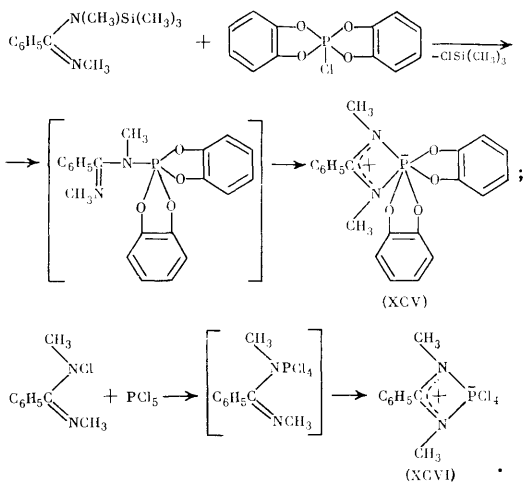
Scheme 15



M = Ag (I), Hg (II), Co (II), Ni (II)

The presence of the degenerate amidine triad, which makes it possible to enter automatically the region of tautomeric processes on the thermodynamic scale, and the existence of methods developed for the investigation of such tautomerism[69] made it possible to obtain important information about the mechanism of the phosphoryl exchange. The phosphoryl migrations in the amidine triad usually occur via an intramolecular mechanism, tentatively via a stage involving the formation of the cyclic intermediate (XCIV) with a trigonal-bipyramidal configuration of the phosphorus atom[73]. Treatment of amidine derivatives with spiro-chlorobis(phenylenedioxy)phosphorane or PCl_5 leads to the formation of the phosphorane derivatives (XCV) and (XCVI) via Scheme 17.[78]

Scheme 17

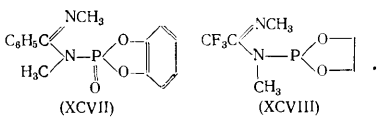


(XCV)

(XCVI)

Although this entails the formation of hexacoordinate and not pentacoordinate derivatives of phosphorus, presumably this type of mutual approach of reaction centres, necessary for intramolecular migrations, can be achieved also in phosphorane intermediates. However, the phosphorane intermediates cannot be detected by physicochemical methods.

It has been concluded[79] that there is no intermolecular exchange of phosphorus-containing groups when compounds (XCVII) and (XCVIII) are heated together. The intermolecular tautomeric process N ⇌ N′ with migration of phosphorus(III) was observed for the latter compound:

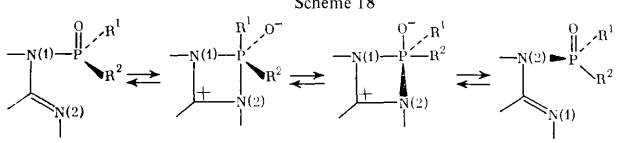


(XCVII) (XCVIII)

The intramolecular mechanism of the phosphoryl migration in amidines has been confirmed by the retention of the spin–spin coupling constants $J(PH)$ and $J(PC)$, whereas in the case of intermolecular migrations these constants would have been averaged out to zero[77].

The geometry of the amidine triad ensures the possibility of only the axial-equatorial disposition of the attacking and leaving nitrogen atoms in the phosphorane intermediate, so that, in conformity with the principle of microscopic reversibility, the latter should undergo ligand exchange via Scheme 18.[69]

Scheme 18

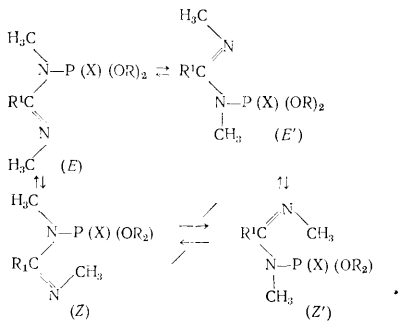


The negative activation entropies (Table 3) indirectly confirm the intramolecular multistage mechanism of the tautomeric transformation, requiring a considerable reorganisation of the molecule. A stereochemical study showed that the tautomeric transformations take place without inversion of the configuration of the phosphorus atom[79]. If the attack on, and elimination of, the nitrogen atom occurred synchronously, for example via an S_N2 mechanism, bypassing the permutation isomerisation stage, this would entail inversion of the configuration of the phosphorus atom. The considerable decrease of the free energy of activation for the tautomeric process (Table 3), involving the incorporation of the phosphorus atom in a dioxa- or benzodioxa-phospholan ring, stabilising the phosphorane intermediate, is consistent with the proposed mechanism[80].

Apart from phosphorylotropism, $E \rightleftharpoons Z$ topomerisation is observed for phosphorylated amidines. The activation energies for these processes can be similar [for example, for compounds (LXXIII), (LXXIV), and (LXXVII); Table 3].

Theoretical calculation of the ^1H NMR spectra for the four-position exchange of topomers ($Z \rightleftharpoons E \rightleftharpoons E' \rightleftharpoons Z'$; Scheme 19) and comparison of the theoretical and experimental spectra made it possible to exclude the possibility of phosphoryl migrations for the Z,Z-isomers:[79]

Scheme 19

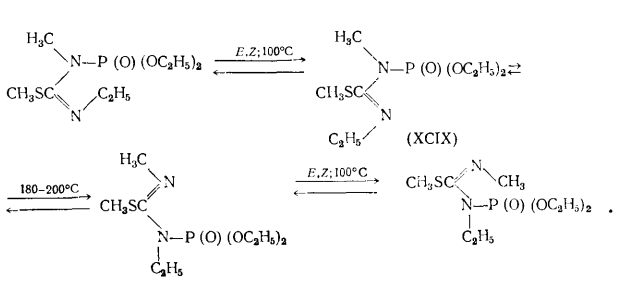


From the standpoint of the intramolecular mechanism, this can be explained by the unfavourable orientation of the unshared electron pair of the imino-nitrogen for a nucleophilic attack on the phosphorus atom.

The free energy of phosphoryl migrations (Table 3) is reduced somewhat when the $CHCl_2$ group at the carbon atom is replaced by a phenyl substituent, which promotes the delocalisation of the positive charge of the intermediate (XCIV). The introduction of electron-accepting substituents at the phosphorus atom greatly reduces the free energy of activation for the tautomeric transformation, which is caused by the increased electrophilicity of the phosphorus.

On passing from phosphorylated amidines to the corresponding derivatives of *S*-methylisothiourea (XCIX), the phosphoryl exchange is observed at a higher temperature (Scheme 20); $\Delta G^{\neq}$ increases to ~26 kcal mol^{-1}:[81]

Scheme 20



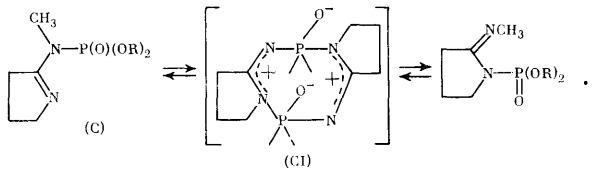
When even one alkyl group at the nitrogen atoms in *S*-alkyl-*N*-phosphorylisothioureas is replaced by hydrogen, the capacity for phosphorylotropism disappears[82]. Prototropic tautomerism occurs in this instance:

$$R^1R^2P(X)NHC(SR^3)=NH \rightleftarrows R^1R^2P(X)N=C(SR^3)NH_2 ,$$

X = O, S; R^1, R^2 = Alk, AlkO; R^3 = Alk, Ar .

The incorporation of one of the nitrogen atoms of the amidine triad in the ring alters the mechanism of the phosphoryl migration[83] (Scheme 21):

Scheme 21



The rate of migration and the half-life of *N*-phosphorylated 2-methylaminopyrrolines (C) depend on the concentration of the solution and the nature of the solvent. On passing to polar solvents, the process is accelerated, which indicates the intermolecular character of the tautomerism; it has been suggested that its mechanism involves the formation of the polar dimeric form (CI) as the intermediate state. The thermodynamic quantities of activation $\Delta G^{\neq} = 28$ kcal mol^{-1} and $\Delta H^{\neq} \cong 21$ kcal mol^{-1} for this type of tautomerism exceed somewhat the values for intramolecular migrations (cf. Table 3), but the activation entropy is the same (−22 e.u.). It is of interest to note that the ratio of the isomers in deuterochloroform and nitrobenzene is approximately the same[83].

The influence of the nature of the heteroatoms between which the phosphoryl or thiophosphoryl groups migrate can be traced in relation to the rearrangements and tautomeric transformations of phosphorylated thioamides and amidines. The 1,3-O → N and N ⇌ N′ shifts take place most readily. They are less susceptible to acid–base catalysis and an intramolecular mechanism involving a four-membered phosphorane intermediate is preferred for such processes with the exception of those cases where this is prevented by the orientation of the unshared electron pair of the imino-nitrogen. With increase of the difference between the electronegativities and apicophilicities of the atoms, the rearrangement cannot always be fitted within the framework of the intramolecular mechanism. The 1,3-S ⇌ N and 1,3-Se ⇌ N shifts can be catalysed by acids and bases. Furthermore, the S(Se)–C bonds are unusually labile in the thio(seleno)-phosphorylated isothioamides, isothioureas, and isothiocarbamates, which is manifested by the ease of the dissociation of the P–S(Se)–C fragment with elimination of the thio- or seleno-phosphoryl group.

V. 1,4-MIGRATIONS AND LONGER-DISTANCE MIGRATIONS

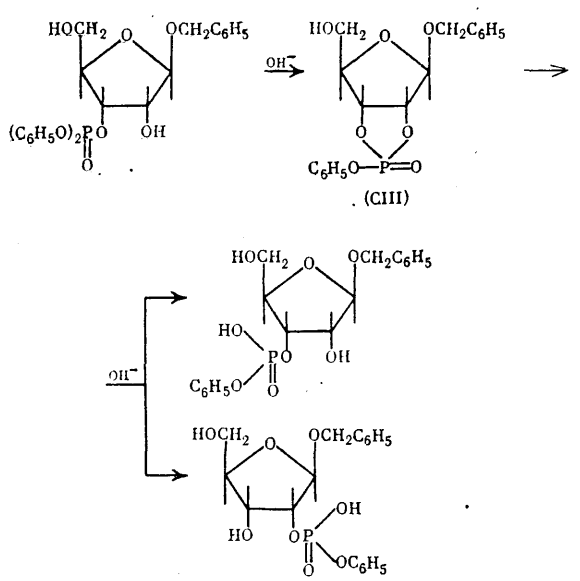
The 1,4-O ⇌ O′ shift of the phosphoryl group was first observed on refluxing an aqueous solution of 2-glycerophosphate (CII) in the presence of H_2SO_4.[84] This rearrangement is reversible[85]:

$$(HO)_2P(O)OCH(CH_2OH)CH_2OH \overset{H^+}{\rightleftarrows} (HO)_2P(O)OCH_2CH(OH)CH_2OH$$

(CII); 10% 90%

According to Khorana[15], the 1,4-O ⇌ O′ transfer of the phosphoryl group proceeds via the cyclic phosphate (CIII), as happens in the mild alkaline hydrolysis of sugar phosphates[86]. Under the influence of hydroxide ions, the phosphate ring can be cleaved on both sides (Scheme 22):

Scheme 22

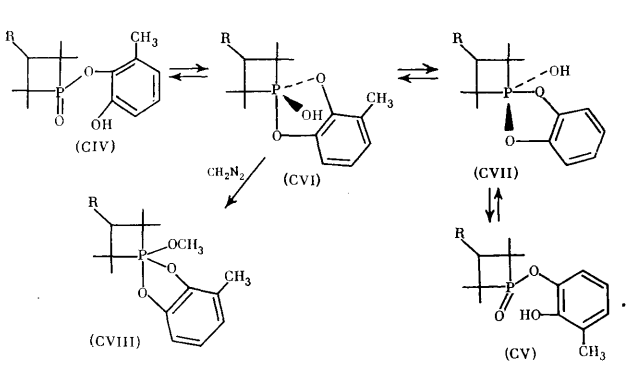


An analogous scheme has been proposed also for the reactions of sugar phosphates with carbodiimides[15,19]. In this case the 1,4-O → O′ shift is also accompanied by the 1,3-O → N shift of the phosphoryl group.

It has been shown recently[87] that the reversible isomerisation of *o*-hydroxyphenyl phosphinates (CIV) to compounds (CV) proceeds via intermediates (CVI) and (CVII) of the hydroxyphosphorane type via Scheme 23.

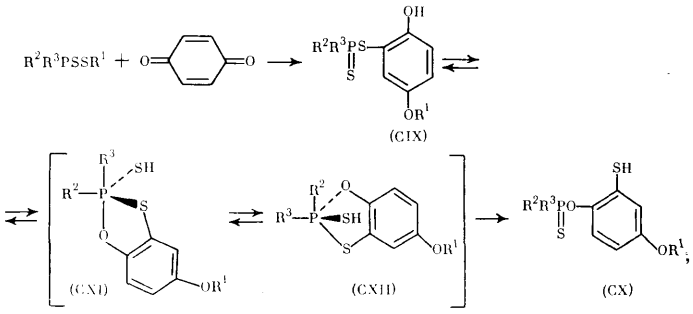
On treatment with diazomethane, the product of the methylation of the hydroxyphosphorane (CVIII) was isolated. The free energy of activation for the transition (CIV) ⇌ (CV) is 17.5 kcal mol^{-1}. When the phosphetan ring in compound (CIV), stabilising the spiro-phosphorane structure[88], is replaced by phenyl groups, the activation energy increases to 24.2 kcal mol^{-1}. The transition from phosphinates to their thio-analogues leads to an increase of the activation energy for the process by 4–5 kcal mol^{-1}. These results suggest that the isomerisation proceeds via a mechanism involving intramolecular nucleophilic substitution at the tetrahedral phosphorus atom:

Scheme 23



The isomerisation of *S*-(2-hydroxyphenyl) esters of phosphorus thioacids probably proceeds analogously via a stage involving the formation of mercaptophosphoranes. Products of type (CIX), formed in the reaction of dialkylphosphorodithioic acids and their silyl esters with *p*-benzoquinone, naphthoquinone, and *N*-benzenesulphonyl-*p*-benzoquinone, isomerise to phosphorothioates of type (CX).[89] This rearrangement proceeds only in one direction—towards the formation of the more acidic thiol (CX) (Scheme 24):

Scheme 24

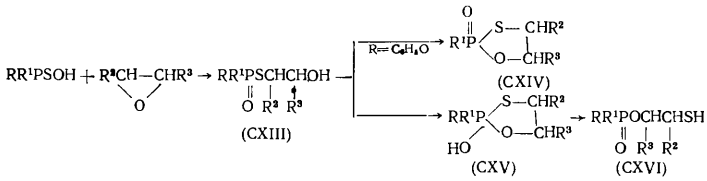


$R^2R^3 = Alk_2, (AlkO)_2, —OC(CH_3)_2C(CH_3)_2O—, —OCH_2C(CH_3)_2CH_2O—$; $R^1 = H, Si(CH_3)_3$.

Diphenylphosphinodithioates rearrange only in the presence of an equimolar amount of triethylamine. The study of the kinetics of the isomerisation of *S*-2,5-dihydroxyphenyl esters of phosphorus dithioacids demonstrated the unimolecular nature of the process[90]. The replacement of the alkoxy-groups at the phosphorus atom in compounds (CIX) by alkyl groups reduces the rate of isomerisation, probably as a consequence of the decrease of the effective positive charge on the phosphorus atom, which hinders the attack on the *ortho*-hydroxy-group. In intermediates with the trigonal-bipyramidal structure (CXI) and (CXII), the alkyl substituents are forced to occupy apical positions. The interactions with three equatorial substituents reduce the apicophilicity of the groups having high steric requirements[91] and hence increases the energy of the intermediates. An appreciable acceleration of the isomerisation is observed for esters of cyclic ω-hydroxy- or ω-mercaptophosphates compared with their acyclic analogues, which may be associated with the cyclic spiro-hydroxyphosphoranes being favoured by energy factors to a greater extent[88]. The influence of the polarity and acidity of the solvents on the rate of rearrangements is very small, which indicates an insignificant charge separation in the transition state of the rate-determining stage.

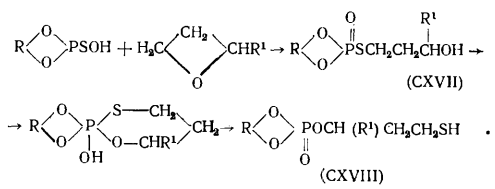
The replacement of a hydrogen atom in compound (CIX) by a trimethylsilyl group greatly stabilises the phosphorodithioate structure. In this case the S → O migration of the thiophosphoryl group can occur only in the presence of a basic catalyst or an excess of a sulphonating agent and the process becomes reversible. Its reversibility can be accounted for by the destabilisation of the phosphorodithioate structure due to the lower energy of the Si—S bond compared with the Si—O bond.

An analogous rearrangement of 2-hydroxyalkyl phosphorothioates was proposed as early as 1968 [92] and the isomerisation products were identified subsequently[93]:



The stability of *S*-(2-hydroxyalkyl) phosphorothioates (CXIII) is determined by the nature of the substituents at the phosphorus atom. Acyclic compounds are fairly stable at room temperature. The rate of their isomerisation increases[94] with decrease of the length of the alkoxy-groups $R = R^1$ in the sequence iso-C_3H_7 < C_2H_5 < CH_3. When the butoxy-group at the phosphorus atom is replaced by the t-butoxy-group, the capacity for rearrangement disappears[95]. In the presence of phenoxy-groups, isomerisation does not occur either, but there is an intramolecular substitution of the phenoxy-group with formation of compound (CXIV).[96] For a mixed environment of the phosphorus atom, the rate of isomerisation increases in the sequence[94] $R^2 = R^3 = H < R^2 = H, R^3 = CH_3 < R^2 = R^3 = CH_3$. A lower mobility of the thiophosphoryl group compared with the phosphoryl group has been observed[97,98]. 2-Hydroxyalkyl phosphorodithioates do not show a tendency towards isomerisation and the latter can be achieved only under more severe conditions[98]. The incorporation of the phosphorus atom in a five-membered ring accelerates the isomerisation to such an extent that 2-hydroxyalkyl phosphorothioates of the 1,3,2-dioxaphosphorinane series[99] can be detected only by ^{31}P NMR. The characteristics of the rearrangement discovered agree with the mechanism involving intermediate formation of the hydroxyphosphoranes (CXV), which are converted into the phosphates (CXVI). The influence of the dioxyalkylene ring at the phosphorus atom on the rate of isomerisation can be explained by the lower energy of hydroxyphosphoranes of type (CXV), containing two five-membered rings, compared with the intermediates containing one five- or six-membered ring. In certain cases the phosphorane intermediates have been detected by ^{31}P NMR.[99]

Conversely, the fact that the *S*-(3-hydroxyalkyl) phosphorothioates and phosphorodithioates, obtained by the addition of acyclic dialkylphosphorothioic and dialkyl phosphorodithioic acids to oxetans, do not isomerise can apparently be explained by the reduced stability of hydroxyphosphoranes with acyclic substituents at the phosphorus atom[100,101]. On the other hand, the products of the addition of five-membered cyclic phosphoromonothioic acids (CXVII) are readily converted into 3-mercaptoalkyl phosphates (CXVIII):[101]

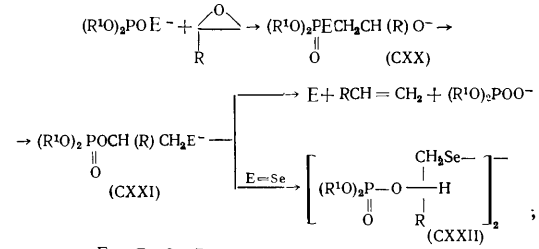


Derivatives of six- and seven-membered cyclic esters of phosphorus acids of type (CXVII) rearrange at 160–180 °C.[102]

The capacity of phosphoryl groups for 1,4-E → O (E = S, Se, or Te) migration is used to deoxygenate epoxides. The products of the interaction of salts of *O*,*O*-dialkylphosphoroselenoic[103] and *O*,*O*-dialkylphosphorotelluroic acids with olefin oxides are the olefins (CXIX), selenium (or tellurium),

and phosphates[104]. Their formation (Scheme 25) involves the rearrangement of the phosphoroselenoates or phosphorotelluroates (CXX):

Scheme 25

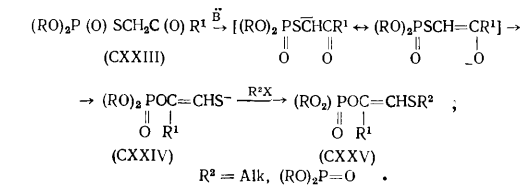


E = Te, Se; R = alkyl or monosaccharide residue.

In the case of salts of phosphonoselenoic acid, the rearrangement products (CXXI) are capable of undergoing also an oxidation-reduction reaction, in which they are converted into the diselenides (CXXII).

When *S*-(2-Oxoalkyl) phosphorothioates (CXXIII) are acted upon by bases, they rearrange to the enol phosphates (CXXIV), which have been isolated in the form of the derivatives (CXXV) [105] (Scheme 26).

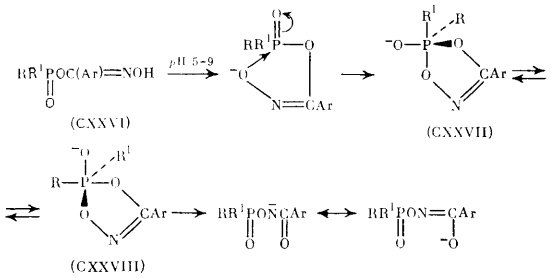
Scheme 26



R^2 = Alk, $(RO)_2P{=}O$.

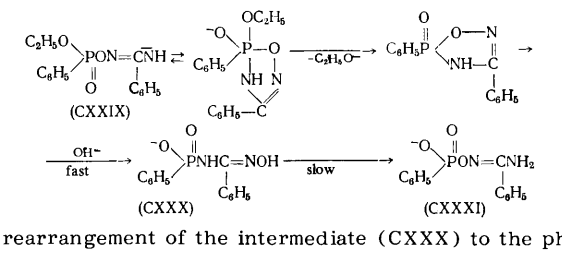
The mechanism of this rearrangement is probably analogous to that of the isomerisation of phosphorylated hydroxamic acids (CXXVI),[106] which proceeds in accordance with Scheme 27 via the intermediates (CXXVII) and (CXXVIII).

Scheme 27



The 1,4-O ⇌ N shift of the phosphono-group occurs in the alkaline hydrolysis of the imidoximes (CXXIX) [107] (Scheme 28):

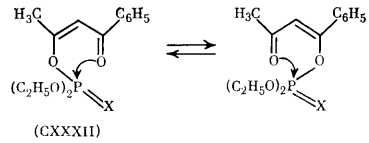
Scheme 28



The rearrangement of the intermediate (CXXX) to the phosphate (CXXXI) is kinetically a first-order reaction.

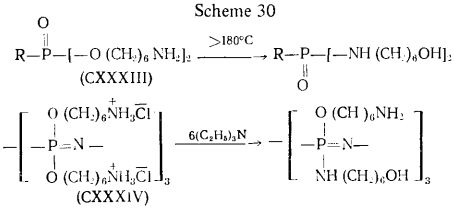
It has been suggested[108] that the reversible rearrangement of the *Z*-topomers of the enol phosphates (CXXXII) derived from 1,3-diketones proceeds via a mechanism involving intramolecular nucleophilic substitution at the tetrahedral phosphorus atom (Scheme 29):

Scheme 29



In contrast to the corresponding acyl derivatives[69], phosphoryl exchange (Scheme 29) is observed only above 150 °C. This is explained by the more stringent steric requirements which must be met by the trigonal-bipyramidal transition state, in which both oxygen atoms must be located in the axial positions. The formation of phosphorane intermediates containing larger than six-membered rings is apparently not a characteristic process.

Scheme 30



Thus the isomerisation of the phosphorylated aminoalcohols (CXXXIII) and (CXXXIV) [109] must be regarded as an intermolecular process.

* * *

The data presented in this review makes it possible to combine the wide variety of rearrangements involving the migration of electron-deficient phosphoryl groups on the basis of the mechanism involving nucleophilic substitution at a tetrahedral phosphorus atom, so that the characteristic features of the phosphoryl migrations can be described in most cases from the standpoint of the "hydroxyphosphorane concept", which constitutes the foundation of the modern interpretation of this mechanism.

The discovery and investigation of phosphorylotropic tautomerism, which will make it possible to examine the fine details of many biochemical processes in which the nature of the elementary reaction step is analogous, has been a great success. The study of the characteristic features and limits of the occurrence of phosphoryl migrations opens new pathways to the synthesis of various new organophosphorus compounds. The development of simple methods of synthesis of imidoyl derivatives of tetracoordinate phosphorus thio-acids and the study of their properties constitute a new field in thiophosphorylation methods.

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Organophosphorus Stabilisers of Polymers: Efficiency and the Mechanisms of Action

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The review is devoted to studies constituting the scientific basis of the search for and selection of highly effective organophosphorus stabilisers of polymeric materials. The physical chemistry of the potential organophosphorus stabilisers and the stabilisers used in practice are examined from this standpoint. The mechanisms of the inhibiting effect of organic phosphites in various compositions are discussed and the relative contributions of the mechanisms considered to the overall inhibiting activity are estimated. The dependence of the reactivity of phosphites on their structure is examined and the quantitative characteristics of the main reactions of phosphites are discussed. The results obtained make it possible to predict the effectiveness of phosphites with different structures as inhibitors of the chain autoxidation and degradation reactions of polymers. The bibliography includes 100 references.

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I. INTRODUCTION

The effective protection of polymeric materials against ageing is an important scientific-technological problem. Numerous studies devoted to the urgent problem of the elucidation of the scientific basis of the ageing and stabilisation of polymers have been published in recent years. They were initiated by the work of Academician N.M.Emanuel'[1,2], who formulated the principles of the ageing and stabilisation of polymers.

Among the wide variety of organic compounds used as stabilisers, organic phosphites (OP) occupy a special place. They are used as stabilisers of polyolefins, raw and cured rubbers, heterochain polymers, and poly(vinyl chloride), and also as inhibitors of the polymerisation of diene hydrocarbons[3]. Numerous investigations in this field have been carried out in Kazan[4-7]. It has been estabilished that the most powerful stabilising antioxidant activity is shown by the aromatic and aromatic alkyl-substituted esters of phosphorous acid which do not colour polymeric materials during their processing and use, exhibit a considerable synergistic effect in mixtures with phenols, are readily blended, are involatile, and their susceptibility to oxidation by molecular oxygen is low.

Qualitative model estimates involving the interaction of phosphites with 1,1-diphenylethyl hydroperoxide[8] and the stable diphenylpicrylhydrazyl radical[9] made it possible to classify phosphites as inhibitors with a combined type of activity: they decompose hydroperoxides, supressing degenerate branching, and can terminate chains by reaction with peroxy-radicals; on the other hand, they are capable of enhancing the activity of catalytic admixtures of variable-valence metals and of blocking weak (as regards degradation) sites in the polymer chain. We shall note the most important phenomenological consequences of such polyfunctionality of organic phosphites.

Firstly, the reactions of organic phosphites with hydroperoxides lead to the intensification (synergism) of the action of typical inhibitors (phenols) in their mixtures with phosphites in the autoxidation of polymers, i.e. under conditions where the main source of radicals is the accumulating hydroperoxides.

Secondly, organic phosphites induce the destruction of peroxy-radicals, which leads to the appearance of induction periods in polymer oxidation processes. As will be shown below, the inhibiting effect of phosphites is associated with the kinetics of their radical-chain oxidation. This is indicated by the broad distribution of the stoichiometric inhibition coefficients for the oxidation reactions carried out in different phases (liquid and solid).

Table 1. Changes in the content of the inner $\diagdown C{=}C \diagup$ bonds $\bar{\gamma}$ in PVC macromolecules on heat treatment in the presence of organic phosphites (353–373 K).[17]

Composition	[OP], mol/mol PVC	τ, h	T, K	$[\eta]_0$, dl g^{-1}	$[\eta]$, dl g^{-1}	$10^4 \cdot \bar{\gamma}$, mol/mol PVC
PVC($\bar{M}_w^0$ = 127 500)	—	—	—	1.23	1.19	1.0
PVC + (I)	0.02	2	100	1.23	1.23	0
PVC + (I)	0.02	8	100	1.23	1.22	0
PVC + (II)	0.02	5	80	1.23	1.23	0
PVC ($\bar{M}_w^0$ = 99 000)	—	—	—	1.02	0.92	1.4
PVC + (I)	0.01	11	80	1.02	1.02	0

Notation: τ is the heat treatment time, $\bar{M}_w^0$ the viscosity-average molecular weight of the initial PVC, and $[\eta]_0$ and $[\eta]$ are the intrinsic viscosities of the PVC solutions before and after ozonisation respectively.

Thirdly, since reactions of organic phosphites with both peroxy-radicals and with hydroperoxides develop simultaneously in the polymer during its oxidation, the observed inhibiting effects under the conditions of the degenerate-branched chain oxidation can be accounted for by the combination of these two mechanisms or their competition.

Finally, the effects of the non-chain inhibition and colour-stabilisation of polymers of phosphites are closely related with the supression of the initiation and development of degradative processes.

The wide variety of the possible mechanisms of the stabilising effect of organic phosphites complicate the theoretical analysis of the process involving the stabilisation of polymers by phosphites. A series of studies have been carried out recently in which the principal properties of organophosphorus compounds as stabilisers of polymeric materials have been established and the principal mechanisms of their inhibiting and colour-stabilising action have been formulated and proved.

The aim of the present review is to analyse the present state of the experimental and theoretical studies (during the period 1973–1983) of the stabilisation of polymers by organophosphorus compounds. The review deals with the principal results of these studies and also with new systems whereby it is possible to represent more fully the kinetic model of the stabilising action of organophosphorus stabilisers.

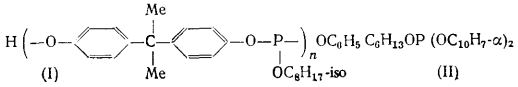
II. STABILISATION OF POLYMERS AT THE DEGRADATIVE PROCESS INITIATION STAGE

1. Poly(vinyl chloride)

The ability of organic phosphites to interact with "weak" sites in macromolecules[10], at which the decomposition of the polymer is initiated in the first place, was observed and demonstrated for the first time in relation to poly(vinyl chloride). As a consequence of the reaction of organic phosphites with the "weak" sections, the degradative processes are inhibited at the initiation stage, which increases the thermal stability of the polymer and leads to the preservation of its initial colour during ageing.

Until recently, in considering the mechanism of the stabilising action of organic phosphites, the complex poly(vinyl chloride) (PVC) dehydrochlorination process was regarded as a single-stage reaction[11–16]. The available literature data therefore make it possible to estimate only the overall effect of phosphites as regards PVC. Minsker et al.[17] published the results of a more detailed study of the influence of phosphite esters on the rate of dehydrochlorination of PVC.[18] The overall result is determined by the superposition of statistical dehydrochlorination processes at a rate w_c, leading to the random formation of isolated double bonds at any site within the macromolecules, and the HCl elimination process leading to the formation of a system of conjugated double bonds at a rate w_n.

It has been established[17] that the action of the phosphites



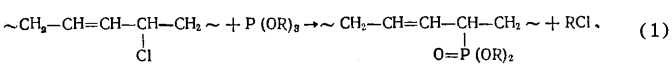
(I) (II)

is manifested by an appreciable decrease (by more than an order of magnitude) of the rate of statistical dehydrochlorination w_c (Fig.1) (with retention or even some increase of the rate of formation of polyene sequences).

This suggests new pathways in the mechanism of the stabilisation of PVC biphosphites: organic phosphites interact with isolated unsaturated bonds >C=C< in the PVC macromolecules. As a consequence, the product of this reaction is not ozonised with subsequent oxidative cleavage; the molecular weight of PVC (a quantitative measure of the statistical dehydrochlorination of the polymer[19]) does not change.

Apart from the data presented in Fig.1, the quantitative "closure" of the inner >C=C< bonds in the polymer chains on heat treatment of PVC in the presence of phosphites constitutes an argument in support of this reaction (Table 1). Among the mechanisms of the stabilising action of organic phosphites in relation to PVC proposed previously, the possibility of the interaction with isolated >C=C< bonds was not taken into account.

The effects associated with the increase of the stability of PVC were usually attributed to the interaction of phosphites with a chlorine atom in the β-position relative to the >C=C< bond in the chloroallyl group[14,20]:



(1)

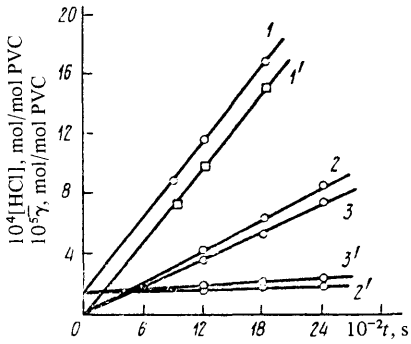
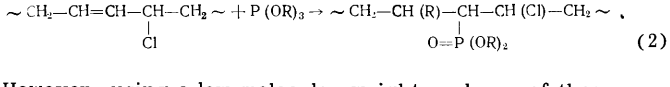


Figure 1. The overall (lines *1*–*3*) and statistical (lines *1′*–*3′*) dehydrochlorination of PVC in the prsence of 0.02 of a mole of phosphites per mole of PVC (448 K, $p = 10^{-2}$ mmHg, $M_w^0 = 127500$, 0.02 of an equivalent of $(C_{17}H_{35}COO)_2Ba$ per equivalent of PVC: 1) and 1′) without phosphite; 2) and 2′) in the presence of compound (I); 3) and 3′) in the presence of compound (II).[17]

The presence and formation of chloroallyl groups in the macrochains was believed to be the main cause of the activation of the HCl elimination process[21–24]. Taking into account the experimentally observed addition of organic phosphites to anomalous groups involving the saturation of the >C=C< bonds, an alternative mechanism was proposed[8]:



(2)

However, using a low-molecular-weight analogue of these groups (4-chloropent-2-ene), it has been shown in relation to model reactions that phosphites (353 K, 100 h; 443 K, 30 h) do not react with the β-chloroallyl groups (neither via the >C=C< bond nor via the C–Cl bond[25]). On the other hand, PVC treated with organic phosphites (with subsequent elimination of the latter) is characterised by a low initial rate of the HCl elimination reaction, the relation being analogous[17] to that described by curves *2* and *3* in Fig.1.

Thus reactions (1) and (2) cannot be adopted as the basis of the mechanism of the stabilising action of organic phosphites in relation to PVC, because this does not reflect the true nature of the phenomenon. This conclusion is particularly valid since it has been shown[18,26,27] that the β-chloroallyl groups are not responsible for the high rate of dehydrochlorination of PVC and that the low stability of

the polymer is caused by the presence in the macromolecules of the carbonylallyl groups ~C(=O)–CH=CH–CH(Cl)~, formed on oxidation of the chloroallyl groups[27]. The interaction of organic phosphites with the carbonylallyl groups in PVC, which leads to a decrease of their content† in the polymer macromolecules (Fig. 2) [28] and hence to a considerable decrease of the initial rate of dehydrochlorination of PVC (Fig. 3), proceeds also at room temperature[28]. Since the organic phosphite is introduced in a large excess relative to the carbonylallyl groups (this corresponds to the real PVC stabilisation conditions), the reaction proceeds in a pseudounimolecular regime and its rate is determined solely by $\bar{\gamma}_0$ (the kinetic plots for the consumption of the carbonylallyl groups can be made linear in terms of semi-logarithmic coordinates). The effective rate constants k for the interaction of organic phosphite with the carbonylallyl in PVC have been calculated for tri-isobutyl phosphite ($k = 0.11 \times 10^{-3}$ s^{-1} at 298 K) together with the parameters of the Arrhenius equation: $E_a = 71.4$ kJ mol^{-1} and $\lg A = 10 \pm 1$.

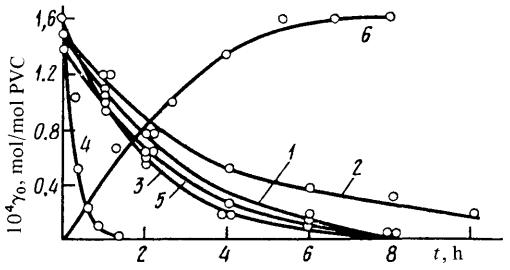


Figure 2. Dependence of the content of ketochlorallyl groups $\bar{\gamma}$ on the time of contact of PVC specimens with $(iso\text{-}C_8H_{17}O)_3P$ at different temperatures (lines *1*–*5*) and on the degradation time (448 K, 10^{-2} Pa) of modified PVC (line *6*); initial content ($10^4\bar{\gamma}_0$, mol/mol PVC): 1) and 6) 1.52; 2)–4) 1.62; 5) 1.42; temperature (K): 2) 289; 3)–5) 298; 4) 313.[28]

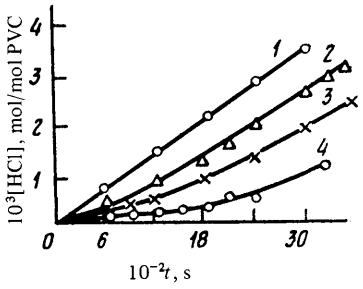
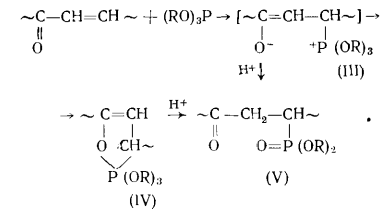


Figure 3. The elimination of HCl from PVC ($\bar{\gamma}_0 = 1.52 \times 10^{-4}$ mol/mol PVC) not containing $(iso\text{-}C_3H_7O)_3P$ (line *1*) and PVC subjected to a preliminary treatment with phosphite at 298 K; treatment time (h): 2) 1; 3) 2; 4) 6.[28]

†The quantitative content of the carbonylallyl groups $\bar{\gamma}$ is calculated from the viscosity-average molecular weight after the alkaline hydrolysis of the $(RO)_3P$-modified polymer[19].

It has been established that the interaction of phosphites with PVC proceeds via the ketovinyl fragment of the carbonylallyl group[29]:



(3)

This is demonstrated by the results obtained in the study of the competitive reactions of the phosphite (tributyl phosphite) with a mixture of methyl vinyl ketone (a model of the ketovinyl fragment) and 4-chloropent-2-ene, which models the β-chloroallyl group (353 K, equimolar reactant ratio). The phosphite reacts selectively with methyl vinyl ketone, while 4-chloropent-2-ene is isolated from the reaction mixture in an unchanged form apart from a certain amount of its dehydrochlorination products—piperylene and HCl.

The final reaction product—butyl 3-oxobutylphosphonate (V), identified by infrared spectroscopy ($\nu_{P=O} = 1250$ cm^{-1}, $\nu_{C=O} = 1730$ cm^{-1}), NMR($\delta_{^{31}P} = +31$ p.p.m.), and elemental analysis, is formed in the presence of a proton donor (HCl in the given reaction) as a consequence either of the protonation of the dipolar ion (III) or the conversion of the intermediate oxophospholen (IV) ($\delta_{^{31}P} = -31$ p.p.m.) into compound (V).[30] Under the real PVC stabilisation conditions, the proton donors can also be either HCl, always present in the polymer during its heat treatment even at relatively low temperatures, or other acid admixtures, H_2O, and phosphite hydrolysis products (alcohols, phenols, etc.).

At the same time during the degradation of the stabilised PVC the rate of evolution of HCl increases[28] to the value characteristic of the initial polymer. The content of the carbonylallyl groups increases in the same way (Fig. 2, curve *6*), which indicates the thermal decomposition of the saturated ketophosphonate groups under the PVC degradation conditions. Treatment of the curve for the accumulation of the carbonylallyl groups during the thermal degradation of the modified PVC in terms of the first-order reaction equation yields $k_{decomp} = (0.93 \pm 0.06) \times 10^{-3}$ s^{-1} at 448 K. At the polymer degradation temperature the ratio $k/k_{decomp} > 10^3$ ($k = 1.8$ s^{-1} at 448 K, calculated from E_a). Thus the high stabilising effectiveness of organic phosphites in relation to the thermal decomposition of PVC is caused, apart from other factors, by the high ratio of the rate constant for the formation of saturated ketophosphonate groups on interaction of organic phosphites with the carbonylallyl groups in PVC and the rate constant for the decomposition of the ketophosphonate groups under the conditions of the thermal degradation of the polymer.

It is significant that the correlation between the activity of phosphites in reactions with α,β-unsaturated ketones and their stabilising effect in PVC made it possible to demonstrate independently that the relatively high overall rate of dehydrochlorination of PVC is in fact determined mainly by the content of the ketochloroallyl structures in the polymer macromolecules.

Thus a new selective phosphorylation reaction, involving the ketovinyl groups of the "anomalous" ketochloroallyl fragments, was discovered for PVC at the degradative process initiation stage. The consumption of the inner double bonds in the carbonylallyl groups, as a result of such interaction of organic phosphite with PVC, results in the breakdown of conjugation in these groups and leads to a sharp decrease of the rate of dehydrochlorination of PVC.

This reaction is in fact the main cause of the inhibition of the formation of polyene sequences inducing the decomposition and colouring of the polymer.

Turning now to the reactions of phosphites with PVC considered in the literature, one should note that, in the inhibition of the decomposition of PVC, the reactions with HCl [31,32] hardly occur under the conditions of the real stabilisation of PVC in the presence of thermostabilisers; the reactions with polyenes $(\sim CH{=}CH\sim)_n$ can develop only under specific conditions[33]; as shown above, the reactions with the β-chloroallyl fragments also fail to make an appreciable contribution to the stabilisation of PVC. All these reactions can be interpreted as concomitant, playing a secondary role in the inhibition of the degradation and colouring of PVC.

2. Polyolefins

The active centres of the degradation process in polyolefins are double bonds, branches in the polymer chains with mobile hydrogen atoms, and carbonyl-containing groups[34].

In the study of polyethylene polymers containing various functional groups, it was found that phosphites are inert[35,36] in relation to hydroxy-groups and double bonds. However, phosphites effectively bind carbonyl groups, reducing their concentration in the initial polymer by a factor of 2–3. Analogous results were obtained in polyethylene (PE) and hexadecane subjected to preliminary oxidation. The introduction of phosphite esters lowers appreciably the intensity of the absorption band of the $>C{=}O$ group in the region of 1720 cm^{-1} in the infrared spectra of the polymer specimens.

The reactivity of phosphite esters in relation to carbonyl groups increases on passing from the full to the acid esters and on replacement of aromatic substituents in the phosphite molecules by aliphatic substituents. Thus, under identical conditions, the concentration of the $>C{=}O$ groups is reduced to the extent of 45, 28, 20.5, and 18% by di-iso-octylphosphorous acid, 2,2'-methylenenbis(6-t-butyl-4-methylphenyl)phosphorous acid, tri-iso-octyl phosphite, and di-iso-octyl phosphite respectively. The observed decrease of the concentration of the $>C{=}O$ groups present in polyethylene, observed after the introduction of phosphites, must be attributed to the chemical interaction of the latter with the carbonyl groups, resulting in the formation of hydroxyphosphonate structures[37].

Thus a general trend in the stabilisation of the colour of polymers by phosphites, namely the deactivation of the reactive centres of macromolecules ("weak" bonds) initiating degradative processes, has been discovered in relation to polymers with fundamentally different decomposition mechanisms (PVC and polyolefins). Reactions of these types involve the chemical modification of macromolecules by polymer-analogue reactions, leading to an increase of the intrinsic stability of the polymer.

It is logical to assume that the observed reactions of phosphites with active anomalous fragments in macromolecules can occur also in the inhibition of the degradation of other polymers containing "weak" bonds of a similar type.

III. STABILISATION OF POLYMERS AT THE OXIDATION CHAIN PROPAGATION AND DEGENERATE BRANCHING STAGES

A problem concerning the stabilisation of polymers, which is important from the standpoint of practical applications, is that of the inhibition of the propagation and degenerate branching of chains in thermo-oxidative degradative processes, responsible for the natural ageing of carbochain polymers.

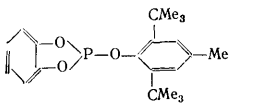
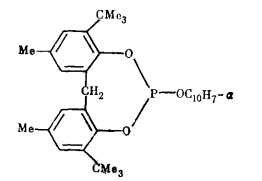
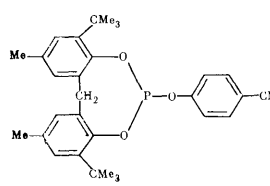
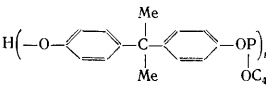
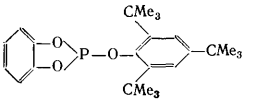
1. Inhibition of Chain Oxidation Processes

The liquid-phase oxidation of phosphorous acid esters by hydroperoxides and peroxy-radicals constitutes a good model for the understanding of their inhibiting effect in the oxidation of polyolefins[38].

(a) *Kinetics and mechanism of the reactions with hydroperoxides.* Quantitative tests of phosphites as hydroperoxide decomposing agents have been carried out by kinetic polarographic and radical trapping methods[39–42].

The kinetics and mechanism of the interaction of phosphorous acid esters depends significantly on their structure. The consumption of hydroperoxides in reactions with the full esters of phosphorous acids obeys first order kinetics with respect to each component. The rate constants for the reactions of phosphites do not vary over a wide range of reaction rates (10^2–10^3) and their stoichiometry is simple (1:1); certain typical values of k are listed in Table 2.

Table 2. The rate constants k, the activation energies E, and the pre-exponential factors A for the reactions of phosphites with cumenyl hydroperoxide (293 K).[38]

No.	Structure of phosphite	10^3k, litre mol^{-1} s^{-1}	E, kJ mol^{-1}	A, litre mol^{-1} s^{-1}
1	$(C_4H_9O)_3P$	83.3	24.7	$3.2\cdot10^3$
2	$(C_8H_{13}O)_3P$	77.9	25.5	$3.8\cdot10^3$
3	$(\alpha\text{-}C_{10}H_7O)_3P$	5.0	37.6	$4.9\cdot10^4$
4		1.3	45.6	$3.2\cdot10^5$
4*	ditto*	3.0 (calc.)	60.3	$6.0\cdot10^7$
5		0.8	58.5	$5.8\cdot10^7$
6		0.8	57.5	$3.8\cdot10^7$
7		12.6	54.8	$1.6\cdot10^8$
8		3.8	58.5	$2.4\cdot10^8$
9	$(PhO)_3P$ **	10.7 (calc.)	34.7	$1.2\cdot10^4$

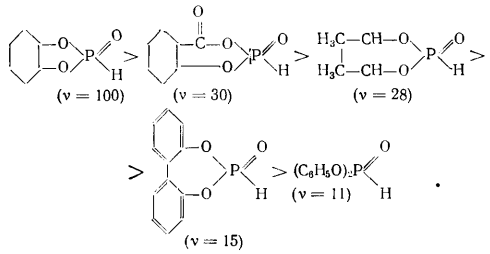
*Data obtained by Humpris and Scott[43].

**E and A obtained[44] for t-butyl hydroperoxide.

The reactions of hydroperoxides with the acid esters of phosphorous acids having the general formula

$$(RO)_2P(=O)H,$$

which are in tautomeric equilibrium with another reactive form, namely $(RO)_2POH$, have been investigated[45]. The rate constants have been calculated from the kinetic equation for termolecular reactions having kinetic orders $n = 2$ and 1 with respect to the hydroperoxide and the acid respectively[46]. The acids can be arranged in the following sequence in terms of the stoichiometric coefficients ν for the consumption of cumenyl hydroperoxide (CHP):



The Arrhenius relation governing the rate constant (20–100 °C) has been derived for *o*-phenylenephosphorous acid (PPA), which decomposes CHP catalytically:

$$k\ (\text{litre}^2\text{mol}^{-2}\,\text{s}^{-1}) = 2.5\cdot 10^{11}\exp(-15.6/RT).$$

Comparison with the ionisation constants determined by potentiometric titration[47] permits the conclusion that the acids having high pK values (>8) do not react; CHP is decomposed only by the strongest acids of the above series (pK < 8). This indicates qualitatively the involvement of the tautomeric forms of the test acids containing phosphorus (III) in the decomposition reaction of CHP as reactive species catalysing its decomposition. The same conclusion has been confirmed by the ^{31}P NMR spectra for PPA ($\delta_{^{31}P}$ = +129, +126 p.p.m.). The presence of two lines at the centre is apparently due to the presence of two conformers with a tervalent phosphorus atom.

Phosphorodithioic acids, having pronounced acid properties, show a high reactivity in reactions with CHP.[48] The study of the consumption of CHP in reactions with phosphorodithioic acids has shown that the latter participate in the reaction with anomalously high stoichiometric coefficients (in the range 7000–25000), which indicates the catalytic character of the decomposition of the CHP. As in the case of dialkyl(aryl) phosphites[47–49], this has been confirmed by the study of the consumption of CHP in the course of its stepwise addition to the reaction system. The rate of decomposition of CHP then remains the same as before, i.e. phosphorodithioic acid is the catalyst. This is also indicated by the absence of an induction period from the kinetic CHP decomposition curve.

The acid-catalysed decomposition of CHP apparently takes place via the mechanism of proton catalysis and is described by a second-order equation with respect to CHP and a first-order equation with respect to the acid[48].

From the standpoint of the effectiveness of the stabilising action of phosphites and acids, the determination of the contributions of the radical and non-radical pathways in the reactions with hydroperoxides is important. The yield of the radicals in the hydroperoxide + phosphite system has been estimated from the consumption of the stable nitroxy-radicals as "counters" of active radicals[40]; it proved to be from 0.02% for aliphatic phosphites to 5% for aromatic phosphites. For phosphorodithioic acids, the contribution of the radical pathway, estimated from the consumption of ionol, increases significantly (to 40%) as a function of structure.

The study of the chemically induced ^{31}P nuclear polarisation (^{31}P CINP) [50,52] in the reactions of phosphites with hydroperoxides has demonstrated unambiguously that the reactions proceed via two parallel (competitive) pathways—non-radical and radical, and that the radical mechanism, which leads to nuclear polarisation, plays a secondary role. Such competition is apparently due to the fact that, for the formation of the primary radical pair $[R'\dot{O}\ HO\dot{P}(OR)_3]$, the reaction of the phosphite with the hydroperoxide should be as a whole either strongly exothermic or it should proceed with a high activation energy, as shown in Fig. 4. The presence of the competitive non-radical pathway therefore enables the reaction to proceed to the formation of molecular products, bypassing the high-energy (endothermic) state of the radical pair[38].

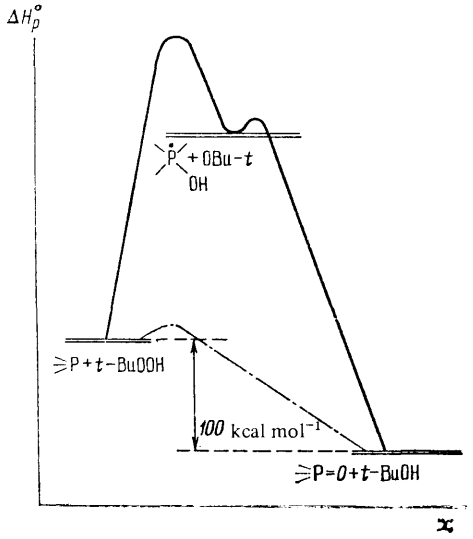


Figure 4. Schematic thermochemical diagram of the possible pathways in the reactions of phosphites with hydroperoxides[38].

The NMR spectra of the products of the reactions of phosphorus dithioacids with hydroperoxides also reflect the effects of nuclear polarisation during periods comparable to the reaction times[53].

Thus, one may conclude that reactions with hydroperoxides via several parallel mechanisms are characteristic of a wide range of esters of phosphorus acids.

(b) *Kinetics and mechanism of the initiated oxidation of organic phosphites.* The reactions of the radicals RO$^{\cdot}$ and $RO_2^{\cdot}$ with phosphites are classical objects of studies in the homolytic chemistry of phosphorus[54,55]; the results available in this field have been subjected to a critical analysis in a review[56]. Trialkyl phosphites are vigorously oxidised by alkylperoxy-radicals $RO_2^{\cdot}$ at 403 K; the oxidation has a chain mechanism and continues until the phosphite is completely exhausted. We shall adopt the conventional term "spontaneous oxidation" of phosphites.

The study of the kinetics of the comparatively weak ^{31}P CINP, observed in the oxidation of trialkyl phosphites under the conditions of an unbranched reaction (azobisisobutyronitrile, O_2, 338 K), demonstrated for the first time[57,58] that this reaction involves phosphorus-containing radicals and their radical pairs. Chemically induced nuclear polarisation occurs only in triethyl phosphite molecules formed in the kinetic chain cross-termination steps:

$$\left[\rangle\dot{P}{-}OR\,\dot{O}_2\,(RO)\,P{\langle}\right] \rightarrow \rangle P^{*}{=}O \quad .$$

Since the same product is formed in the chain propagation steps

$$RO_2^{\cdot} + \rangle P \rightarrow \rangle\dot{P}{-}O_2R \rightarrow \rangle P{=}O + \dot{O}R \;;$$

$$RO^{\cdot} + \rangle P \rightarrow \rangle\dot{P}{-}OR \rightarrow \rangle P{=}O + \dot{R} \xrightarrow{O_2} RO_2^{\cdot} \text{ etc.},$$

the molecules of phosphate with polarised nuclei are actually greatly "diluted" by the molecules of phosphate arising in the chain propagation reactions. Kinetic proof of this mechanism of the CINP has been presented[59] and the causes of the low polarisation coefficient (chain reaction with long chains) have been stated.

In order to discover the principal trends in the "spontaneous oxidation" of phosphites, the rates w_p of their chain oxidation have been analysed as a function of the rate of initiation w_i and the concentration of phosphites. The chain length ν is appreciably reduced (from ~10^4 units for trialkyl phosphites to 5–130 units for aromatic phosphites, particularly when shielded phenoxy-fragments are introduced into the phosphite molecule). Furthermore, on passing from aliphatic to aromatic phosphites, the $w_p \cong w_i^{1/2}$, relation observed for the former, changes to a relation of the type $w_p \cong w_i$, i.e. there is a change in the mechanism of the oxidation chain termination: the bimolecular chain termination is replaced by linear termination by secondary phenoxy-radicals. The latter can be formed via substitution reactions from kinetically unstable phosphoranyl radicals:

$$(ArO)_3\dot{P}OR \rightarrow (ArO)_2POR + ArO\dot{} \xrightarrow{RO_2^{\cdot}} \text{chain termination.}$$

This is precisely why the chemically induced ^{31}P nuclear polarisation is not observed in the chain oxidation of aromatic phosphites.

The appearance of phenoxy-radicals in the initiated phosphite oxidation reaction generates an additional chain transfer mechanism [taking into account the main $RO_2^{\cdot}(RO^{\cdot})$ + phosphite chain transfer pathway]; thus the addition of unsubstituted phenol stimulates the overall phosphite oxidation reaction.

(c) *Kinetics of the inhibition of oxidation processes by organic phosphites.* We shall examine the kinetic parameters, obtained recently characterising the effect of organic phosphites on the initiated oxidation of polyolefins in the solid phase and in the melt[57,60–63], as well as model oxidation reactions of low-molecular-weight substrates.

Fig. 5 presents the kinetic curve for the absorption of oxygen, typical for the phosphite-inhibited oxidation of both model hydrocarbons (styrene, tetralin, benzaldehyde, and low-molecular-weight polyethylene) and solid polyolefins (low-pressure polyethylenes, isotactic polypropylene). The inhibition parameters (determined from the O_2 absorption kinetics) in various substrate + oxygen + initiator + organic phosphite systems are presented in Table 3. The full organic phosphite esters terminate kinetic styrene and tetralin oxidation chains faster by more than an order of magnitude than a typical inhibitor (ionol). The rate constants for the reactions of the polymeric radicals $RO_2^{\cdot}$ with phosphites are comparable to (in solid polypropylene) or even smaller than (in fused polyethylene) the constants k_7 for the known amine and phenolic antioxidants as well as nickel and zinc carbamates. After the introduction of shielded phenoxy-groups into the phosphite molecule, the chain termination rate constant (k_7 or k_7/k_2) almost always increases; however, at the same time there is an increase in the stoichiometric inhibition coefficient f.

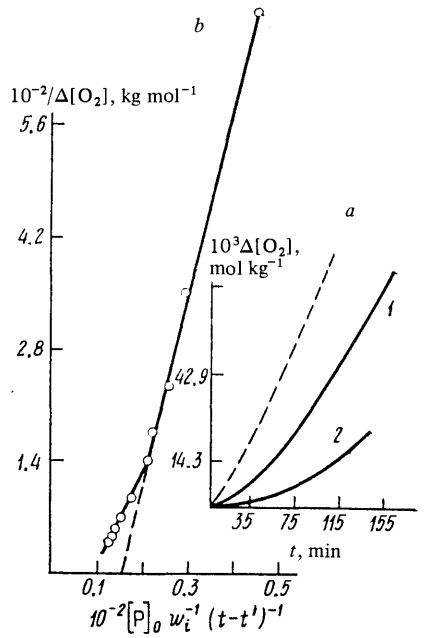


Figure 5. *a*) Kinetics of the initiated oxidation of polypropylene ($w_i = 3.8 \times 10^{-7}$ mol kg^{-1} s^{-1}, 358 K, p_{O_2} = 650 mmHg) in the presence of 1×10^{-2} [of a mole?] (line *1*) and 3×10^{-2} [of a mole?] (line *2*) of triphenyl phosphite (the dashed line represents the kinetics in its absence); *b*) linear kinetic plot in terms of the variables of the equation quoted by Denisov[64].

Table 3. Kinetic characteristics of the reactions of peroxy-radicals with organic phosphites[42].

Composition of medium***	$(C_6H_5O)_3P$		$(Me\text{-}C_6H_3(CMe_3)\text{-}O)_3P$		$(H_{19}C_9\text{-}C_6H_4\text{-}O)_3P$	
	f	$\lg k_7$	f	$\lg k_7$	f	$\lg k_7$
Solid PE at 390 K (MW 6×10^4; $\alpha = 0.82$)	0.63	3.63*	0.97	3.83*	—	—
Fused PE at 1170 K (MW 2350)	—	—	0.63	3.43*	—	—
Solid isotactic polypropylene at 358 K (MW 4.9×10^5; $\alpha = 0.80$)	$6.6 \cdot 10^{-2}$	3.85*	0.12	4.49*	—	—
Styrene + chlorobenzene (50 vol.%) at 323 K	$1 \cdot 10^{-2}$	4.86	$6.3 \cdot 10^{-2}$ ($8 \cdot 10^{-2}$)	4.76 (4.62)**	0.27	4.76
Tetralin + chlorobenzene (50 vol.%) at 323 K	$1.5 \cdot 10^{-2}$	5.00	$4.9 \cdot 10^{-2}$	5.49	—	—
Benzaldehyde (0.2 M) + chlorobenzene at 323 K	0.5	6.20	2.0	6.49	3.4	6.74

*The rate constant is effective; the measured ratio k_7/k_2 is quoted.

**The parameters were evaluated by the computer modelling of the kinetics of the absorption of O_2.

***α = degree of crystallinity.

Direct quantitative estimates of the effectiveness of phosphites have convincingly demonstrated the validity of the early idea[4-7] that aromatic phosphites with shielded (or electron-donating) substituents should be more effective polyolefin stabilisers.

The interaction of aliphatic phosphites with peroxy-radicals proceeds with formation of alkyl radicals, which are actively involved in the oxidation chain propagation (i.e. powerful chain terminating agents—secondary radicals, for example aryloxy-radicals—are not formed). This is why the polymer is oxidised at a high rate even when the constant k_7 for trialkyl phosphite (for example, tri-iso-octyl phosphite) is greater than the constant k_2 for the chain transfer to the substrate[42].

In order to identify the reaction products of aromatic phosphites in the oxidation of a polyolefin, for example, polyethylene, the experiments were interrupted[61] at the end of the inhibited oxidation period (when the oxidation passed to the regime with the usual initiated reaction), while the low-molecular-weight products were extracted by carbon tetrachloride. Absorption frequencies characteristic of the C–O–P linkage and the aromatic ring were detected in the infrared spectra of the oxidised polymer; the inhibitor conversion products extracted from polyethylene contain the P=O and C–O–P fragments. This result can be explained qualitatively within the framework of the mechanism proposed:

$$R'OOR' \xrightarrow{w_i} R'O^{\cdot} \xrightarrow{RH} R^{\cdot},$$

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \xrightarrow[k_2]{RH} R^{\cdot},$$

$$R^{\cdot} + RO_2^{\cdot} \rightarrow \text{products},$$

$$RO_2^{\cdot} + \text{—}P^{III}\text{—} \xrightarrow{k_7} \text{—}P^{V}(=O)\text{—} + RO^{\cdot}; \quad (4)$$

$$RO^{\cdot} + \text{—}P^{III}\text{—} \rightarrow \left[RO\text{—}\dot{P}\text{—}\right] \rightarrow RO\text{—}P^{III}\text{—} + ArO^{\cdot}, \quad (5)$$

$$ArO^{\cdot} + RO_2^{\cdot}\ (ArO^{\cdot}) \rightarrow \text{products}.$$

The mechanism postulates that the phosphite is oxidised by the $RO_2^{\cdot}$ radical to the phosphate [reaction (4)]; in addition, a reaction takes place in which a phosphite molecule is "inserted" in a seocndary alkoxy-macroradical $RO^{\cdot}$ with elimination of a phenoxy-radical (aryloxy-radical) [reaction (5)]. In conformity with the evidence presented by Denisov[64], the mechanism also includes the oxidation chain termination via the reaction between the alkyl macroradical ($\dot{P}$) and the peroxymacroradical ($PO_2^{\cdot}$).

The marked weakening of the inhibiting activity of tri-(6-t-butyl-4-methylphenyl) phosphite (VI) in fused polyethylene (Table 3) is apparently associated with the fact that diffusion- and structure-dependent hindrance, caused by the specific features of the solid phase, diminishes and the contribution of new chains, arising via the reaction of secondary phenoxy-radicals (from the phosphite) not only with the inhibitor but also with the polymer macromolecules, increases. In the liquid phase the coefficient f decreases still more markedly; in this case the chain "spontaneous oxidation" reaction of the phosphite plays an active role, creating powerful additional channels for the consumption of the inhibitor. In fact, in the inhibition of the oxidation of both styrene and tetralin, the coefficient f increases from $(1-1.5) \times 10^{-2}$ for $(PhO)_3P$ to $(5-6) \times 10^{-2}$ for the "shielded" phosphite (VI), i.e. in proportion to the reciprocal of the "spontaneous oxidation" chain length for these phosphites (the corresponding values of ν are 0.6×10^2 and 0.2×10^2 respectively) in *o*-dichlorobenzene[59]. Computer calculation of the rate of consumption w_p of the inhibitor (VI) in styrene showed[63,65] that it exceeds by an order of magnitude the "specified" rate of initiation w_i. Thus the phosphite is consumed via a chain mechanism with a chain length $\nu = 0.1 \times 10^2$. (The value obtained is close to the value of ν determined independently in experiments on the initiated oxidation of the same phosphite.)

If the effectiveness of the inhibition of oxidation by phosphites is determined by comparatively large rate constants k_T for their reactions with peroxy-radicals, then the duration of the stabilising action of the phosphites depends on the intensity of their competitive (coupled) chain "spontaneous oxidation", which determines the stoichiometric coefficient f of the inhibition. The set of such closely related processes is a specific feature of the inhibiting activity of organophosphorus oxidation inhibitors. Knowing these characteristics of the behaviour of organic phosphites, it is possible to predict the most effective regimes for the stabilisation of polyolefins (under storage and operating conditions) when the "spontaneous oxidation" of phosphite is suppressed and the duration of their stabilising action increases significantly.

Thus, in the oxidation reactions of both low-molecular-weight hydrocarbons and polyolefins, the most effective inhibition mechanism involves the interactionof the phosphites with peroxy-radicals.

The results presented above show that, in the presence of aromatic phosphites, the oxidation of polyolefins (in the solid phase and in the melt) and model hydrocarbons is a chain reaction with linear chain termination by phosphite molecules, i.e. typical mechanisms of the action of oxidation inhibitors operate.

2. Molecular Reactions of Organic Phosphites with the Products of the Thermal and Thermo-oxidative Degradation of Polymers

Under the conditions of an advanced polymer oxidation process, the non-chain inhibition reactions—via the interaction of phosphites with active functional groups and molecular decomposition products (peroxides, carbonyl-containing groups, isolated and conjugated double bonds, etc.)—also acquire a considerable importance.

The development of reactions of organic phosphites with the C=O groups formed in the thermo-oxidative degradation of polymers has been established for polyolefins[66,67], polychloroprene[68], etc.

Thus, under the conditions of the autoxidation of polyethylene in the presence of phosphite esters, a considerable retardation of the formation of carbonyl groups is observed compared with the polyethylene specimen not containing the organophosphorus additive[36]. It is noteworthy[66,67] that the polymer is then phosphorylated: the infrared spectra of the polyethylene reprecipitated after oxidation contains the absorption frequencies of the phosphoryl groups corresponding to the products of the reactions of phosphites with carbonyl compounds. The effectiveness in the reactions with carbonyl groups increases with increase of the concentration of the organophosphorus compound. When polyethylene contains ≥5 wt.% of the organophosphorus additive, the spectrum altogether fails to show the absorption lines of C=O groups in the course of 900 h.[66]

The ability of organophosphorus compounds to interact with C=O groups is correlated with the improvement of the operating characteristics of the polymer.

Experimental evidence for deactivation, under the influence of phosphites, of the reaction centres formed at the stage of extensive degradation of poly(vinyl chloride) and responsible for its colour is provided by the decrease of the rate

of dehydrochlorination and the weakening of the colour of the partly dehydrochlorinated PVC.[33] At the beginning of its heat treatment in the presence of phosphites, the latter reacts vigorously with the reaction centres present in the polymer; subsequent heat treatment leads to a monotonic increase of the amount of phosphorus in the degraded PVC as a consequence of the interaction of the phosphite with the active groups in the polymer as they are formed.

The observed phosphorylation of PVC must be attributed primarily to the interaction of the phosphites with the oxygen-containing fragments [reaction (3)]. When polyconjugated structures (chromophoric groups) arise in the macromolecules, organic phosphites weaken the colour of the polymer by breaking the conjugation chain ("symptomatic" stabilisation).

When the binding of the HCl evolved in the degradation of PVC and the formation of complexes of HCl with the double bonds intensifying the colour of the polymer are not effective, phosphites are capable of binding the HCl, which also leads to a weakening of the dehydrochlorination process and the stabilisation of the colour of the polymer[33]. The efficiency of the stabilising action of phosphites, due to their combination with HCl, depends on the degree of their dealkylation under the influence of HCl and the composition of their dealkylation products; the complete dealkylation, characteristic of $(RO_3)P$, leads to the formation of acid products of the type of $ROP(OH)_2$ and H_3PO_3, which accelerate the dehydrochlorination of PVC; aromatic phosphites $(ArO)_3P$ do not react with HCl. Mixed phosphites of the type of $ROP(OAr)_2$ are the most effective stabilisers of PVC; their interaction with HCl results in the formation of only $(ArO)_2P(=O)H$, which are inert on further exposure to HCl.[33]

It is significant that, under the conditions of the inhibition of advanced degradative processes, phosphites are capable of functioning as a "depot" of stabilisers[2], forming under the influence of dealkylating agents (the polymer decomposition products, particularly H_2O, HCl, RCOOH, etc.) the corresponding diaryl(alkyl) phosphites. The latter are active *in statu nascendi*, i.e. their main bulk exists in a bound state and the active form of the stabiliser is evolved from the latter gradually. This is particularly likely since dialkyl(aryl)phosphorous acids are extremely reactive in relation to free radicals[69,70], conjugated polyene systems[71], carbonyl compounds[72,73], etc.

Overall, the general trends in the structural selectivity of phosphites in reactions with the active centres for the decomposition and colouring of polymers have been discovered[74]; in relation to electrophiles (hydroperoxides, carbonyl-containing compounds, activated unsaturated structures, H_2O, HCl, etc.), the reactivity of phosphites decreases in the sequence

$$(RO)_3P > (RO)_2POAr > ROP(OAr)_2 > P(OAr)_3 .$$

Phosphites containing electronegative substituents R in the ester group are effective in reactions with polyene systems $(\sim CH{=}CH\sim)_n$ with $n \geq 4$, which are powerful nucleophiles.

Thus the study of the mechanism of the stabilisation of polymers by phosphites at advanced stages of the degradation makes it possible to predict effective procedures for the secondary stabilisation of polymeric products, i.e. the suppression of the processes which alter significantly the operating properties of the polymer. This means that phosphites are not merely the usual auxiliary additives; they acquire an independent and sometimes a decisive importance.

IV. THE IMPROVEMENT OF THE EFFECTIVENESS OF ORGANOPHOSPHORUS STABILISERS (SYNERGISM)

A distinctive property of organophosphorus stabilisers is their ability to exhibit synergistic effects in a mixture with other additives[3]. The synergism can be achieved either as a result of the enhancement of the functions of organophosphorus stabilisers as inhibitors of free-radical oxidation or by increasing their contribution to the non-chain inhibition processes. We shall consider certain examples of such synergism.

1. Kinetics and Mechanism of the Synergism in the Action of (M + P) Pairs in the Inhibition of an Initiated Oxidation Reaction

The phenomenon of a sharp intensification of the effectiveness of aromatic phosphites as inhibitors of the initiated oxidation of low-molecular-weight hydrocarbons (styrene, tetralin) and polyolefins under the influence of quadrivalent titanium compounds[75] and transition metal acetylacetonates $Macac_n$, where M = Co^{2+}, VO^{2+}, Cr^{3+}, Ni^{2+}, etc., has been observed[76]. The most important general properties of this phenomenon have been established.

In the presence of metal acetylacetonates the dependence of the induction period on the phosphite concentration has a "critical" character (Fig.6). This agrees well with the hypothesis[1] of the formation of a new, more effective inhibitor—a complex of the metal ion with the phosphite, which reacts vigorously with the peroxy-radical.

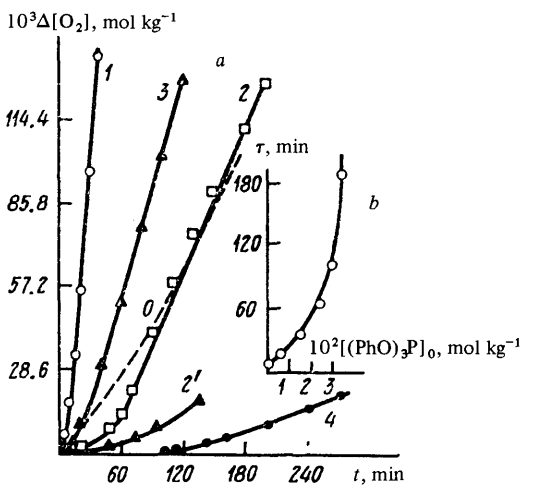


Figure 6. *a*) Kinetic curve for the absorption of oxygen by solid polypropylene (358 K, p_{O_2} = 650 mmHg, $w_i = 3.8 \times 10^{-7}$ mol kg^{-1} s^{-1}) in the presence of 3×10^{-3} mol kg^{-1} (line *1*) or 6×10^{-4} mol kg^{-1} (line *3*) of $Coacac_2$, of a mixture of 3×10^{-3} mol kg^{-1} of $Coacac_2$ + 3×10^{-2} mol kg^{-1} of $(PhO)_3P$ (line *2*), of a mixture of 6×10^{-4} mol kg^{-1} of $Coacac_2$ + 3×10^{-2} mol kg^{-1} of $(PhO)_3P$ (line *4*), and of 3×10^{-2} mol kg^{-1} of $(PhO)_3P$ (line *2'*); 0) curve for initiated oxidation in the absence of the metal complex and phosphite; *b*) dependence of the observed induction period τ on the initial $(PhO)_3P$ concentration in the oxidation of polypropylene in the presence of an initiator and 6×10^{-4} mol kg^{-1} of $Coacac_2$.[76]

Using the "critical" concentration of the phosphite, the rate constant k'_7 for the inhibition of the oxidation of styrene by the coordinated phosphite was obtained and was found to be much greater than not only the constant k_7 for the free phosphite but also the constant k_7 for the metal acetylacetonate and for the familiar reference inhibitor (ionol). The "activation" of the phosphite as an inhibitor when it is coordinated to the metal ion is satisfactorily confirmed by the computer calculation of the kinetics of the oxidation of styrene and its inhibition by the metal ion–phosphite composition[65,77].

The chain oxidation reaction passes from the region of the rapid distinctly catalytic process (in the presence of metal ions) to the region of a slow process with linear chain termination by the molecules of the coordinated phosphite. The study of the kinetics of this process made it possible to determine the quantitative parameters of the observed synergism[76]. Analysis of these parameters shows that the catalytic oxidation of polypropylene by metal ions is suppressed most effectively by the phosphite for the ratio $[M]/[P] \leq 6 \times 10^{-2}$, i.e. when the metal concentration in the polymer does not exceed 0.02 wt.% and the phosphite concentration is close to values usually employed (0.5–1.0 wt.%). The manifestation of "critical" concentrations is in fact characteristic of this range of [M]/[P] ratios.

The series of the relative "synergistic" activities of metal ions in compositions with phosphites in styrene, tetralin, and solid polypropylene have been established on the basis of the analysis of the quantitative parameters of the oxidation inhibition process[38]; overall they have the same direction in terms of the "strength" of the synergism, which implies that the nature of the observed synergism is the same in all cases regardless of the type of substrate oxidised. It has been discovered that the "strongest" compositions are those (based on $Niacac_2$) in which the organometallic component exhibits only a weak catalytic activity; this tendency can be used as a rule in selecting other compositions.

The general characteristics of the behaviour of the kinetically labile metal–phosphite complexes established in oxidation systems with participation of peroxy-radicals make it possible to predict the activity of a new class of oxidation inhibitors—individual stable metal complexes containing molecules of organic phosphites as the main ligands. A remarkable feature of these complexes, for example, the copper(I) complexes is, according to the literature[78–83], a significant increase of the stoichiometric inhibition coefficient, which implies that the reactions involving the additional consumption of the phosphite bound in the complex by a chain process are virtually suppressed. The study of the initiated oxidation of styrene and solid isotactic polypropylene has shown[78] that the copper(I) phosphite complexes (CuP) are more effective than the free non-coordinated phosphite; the quantitative characteristics of the inhibiting action of these complexes have been calculated and it has been shown that the termination of the kinetic oxidation chains by the inhibitor molecules involves the oxidation of the coordinated phosphite without change in the degree of oxidation of the central metal ion.

It is noteworthy that the reactions of the metal complex inhibitor or the products of its reaction with the polymeric hydroperoxide are important for polypropylene undergoing oxidation in the presence of an initiator. It has been found[78] that these reactions have a radical mechanism and proceed at high rates. They are in fact responsible for the "inhibitor $\rightleftharpoons$ catalyst" transition in the kinetic behaviour of the copper(I) phosphite complex observed in the course of the oxidation. In other words, when CuP is used favourable possibilities are created for controlling the regime of the polymer stabilisation under natural conditions, when there is no initiator (controlled stabilisation under uncontrolled conditions). An increase of the duration of the stabilising action of the CuP complexes can be achieved primarily by suppressing the hydroperoxide initiation channel. Below we shall consider a number of experimental facts confirming this idea.

2. The Synergism of Mixtures of Phosphite Complexes with Aromatic Amines

The aromatic amines *p*-toluidine, *o*-toluidine, and diphenylamine have been investigated[81] as "deactivators" of the ROOH groups, but the expected effect was observed only for *p*-toluidine (T) (we may note that *p*-toluidine inhibits weakly the oxidation of polypropylene).

Fig.7 presents as an example typical time variations of the absorption of O_2 in the system comprising polypropylene undergoing oxidation to which T + $Cu[(PhO)_3P]Cl$ or CuP mixtures have been added, the molar concentration ratios of the latter amounting to 0.5–2.0. The character of these relations indicates the occurrence of synergism and at the same time the actual suppression of the secondary processes involving the initiation of the oxidation of polypropylene. The synergistic effect depends in a definite manner on the inhibitor/deactivator ratio and on the concentration of the metal complex additive.

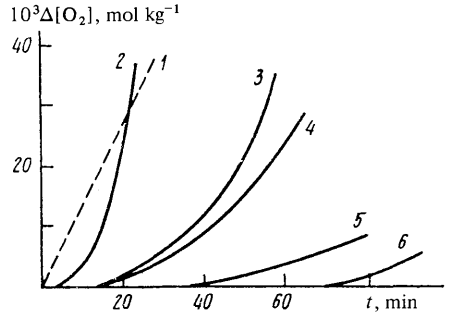


Figure 7. Kinetic curves for the absorption of oxygen by polypropylene undergoing oxidation (358 K, $w_i = 2.5 \times 10^{-6}$ mol kg^{-1} s^{-1}, $p_{O_2} = 650$ mmHg) in the absence of an inhibitor (line *1*) and in the presence of inhibitors: 2) [CuP] = 5×10^{-3} mol kg^{-1} and [T] = 2.5×10^{-3} mol kg^{-1}; 3) [CuP] = 5×10^{-3} mol kg^{-1} and [T] = 1×10^{-2} mol kg^{-1}; 5) [CuP] = 1×10^{-2} mol kg^{-1} and [T] = 1×10^{-2} mol kg^{-1}; 6) [CuP] = 1×10^{-2} mol kg^{-1} and [T] = 5×10^{-3} kg^{-1}.[78]

Thus, when [CuP] = 1×10^{-2} mol kg^{-1} and for the ratio [CuP]/[T] ≥ 1, there is a sharp increase of the induction period τ (see curves *5* and *6* in Fig.14); when [CuP] = 5×10^{-3} mol kg^{-1} for the ratio [CuP]/[T] = 0.5–2.0, the synergism is either much weaker (curves *3* and *4* in Fig.14) or is not observed at all (curve *2* in Fig.14). If the concentration of the amine exceeds that of the phosphite complex, the induction period, defined here as the time during

which $\Delta[O_2]$ reaches 5×10^{-3} mol kg^{-1}, at a constant overall mixture concentration [CuP] + [T] = 1.5×10^{-2} mol kg^{-1} diminishes as a consequence of the probable displacement of the phosphite as a ligand from the coordination sphere of the copper ion by the amine. This means that, in the presence of synergistic amine additives, the phosphite complex retains its key function—it terminates the kinetic chains in the oxidation of polypropylene.

The maximum value of f for the conditions [CuP] = 1×10^{-2} mol kg^{-1} and [CuP]/[T] = 2 amounts to 0.7, which exceeds by a factor greater than two the corresponding value of f obtained for CuP without an amine additive.

An inhibition mechanism has been proposed, in which the amine occupies a free site in the coordination sphere of the ion after the phosphite has been "converted" in the kinetic oxidation chain termination steps into phosphate incapable of coordination; the secondary complexes formed actively decompose the polymeric hydroperoxide to products which do not participate in the polymer oxidation chain propagation reactions. The mechanism has been confirmed kinetically and by analysing the reaction products[77].

3. The Functions of Organophosphorus Compounds in Polymer Systems Containing Phenolic Antioxidants

The effective stabilisation of polymers under the conditions of the development and branching of degradative processes is observed when phosphites are used also in combination with other additives, in the first place[84-86] polymer oxidation inhibitors (phenolic antioxidants). By binding the $RO_2^{\cdot}$ radicals, the latter suppress the spontaneous oxidation reactions of phosphites and thereby enhance the functions of phosphites as inhibitors of non-chain oxidation processes and colour stabilisers.

Not only phosphites[85,86] but also diarylphosphorous and diarylphosphorodithious acids[53] exhibit a high effectiveness with mixtures of phenolic antioxidants. The stabilising effect of the organophosphorus compounds then obtains primarily as a result of the decomposition by the latter of the hydroperoxides ROOH as well as other reactive molecular polymer decomposition products which have accumulated in the polymer undergoing oxidation. The synergistic effect (determined from the colour stability index) in the presence of binary mixtures of phosphites and phenolic antioxidants is characterised by a prolonged retention of the initial colour by such polymer systems and is due to the ability of the phosphites to decompose the chromophores formed as a result of the reactions of phenols and the associated admixtures, in particular of coordination-unsaturated metal ions[86-89].

It has been shown that a characteristic feature of the phosphites[90-92] and phenolic antioxidants[93-96] is the formation of coloured complexes with vanadium, titanium, etc. chlorides (modelling the components of the catalytic polymerisation systems), which are the cause of the appearance of colour in high-density polyethylene immediately after the introduction of phosphite and phenolic stabilisers (inert medium).

In the presence of phosphites, the colour stabilisation effect under the conditions of atmospheric ageing is due to the high rate of the subsequent inner-sphere hydrolysis of the phosphite coordinated to the metal (K_{hydr} = 10 s^{-1}), which leads to the formation of colourless products.

The effectiveness of the colour stabilisation is determined mainly by the competition between the phosphites and phenolic antioxidants in the formation of complexes with variable valence metals[91]. Thus chemical equilibrium is established in the ternary phosphite–bisphenol–metal chloride system (subject to the condition of similar stability constants of the phenolic and phosphite metal complexes) at comparable concentrations of the phosphite and bisphenol; the equilibrium shifts towards the formation of the phosphite complex in the presence of an excess of the phosphite:

$$VOCl_3 + L' \rightleftarrows VOCl_3 \cdot L' \rightleftarrows VOCl_3 \cdot L'' + L'$$

where L′ is the bisphenol and L″ the phosphite. A similar complex is formed after the introduction of an excess of the phosphite (2-ethylhexyl phosphite) into a hydrocarbon solution of the phenol [2,2′-methylenebis(6-t-butyl-4-methyl phenol)] complex of $VOCl_3$; the infrared spectra of the reaction mixture show an intense band in the region of the absorption of the hydroxy-group.

Analogous features of the behaviour of phosphites are observed also in a polymer system. Thus the effectiveness of the colour-stabilising action of phosphites in relation to high-density polyethylene depends on the stability of the phenolic metal complexes; when the stability constant of the complex of 2,2′-methylenebis(6-t-butyl-4-methylphenol) and $VOCl_3$ is $K_{st} = 8.7 \times 10^4$ litre mol^{-1}, an excess of the phosphite relative to the phenol concentration is necessary (by a factor of 3–7); for the higher stability constant $K_{st} = 3.5 \times 10^6$ litre mol^{-1} of the complex of 2,2-thiobis-(4-methyl-2-methylbenzylphenol) and $VOCl_3$, the required phosphite concentration increases by a factor of 5–10.

The greatest effectiveness in neutralising the action of coordination-unsaturated metals is to be expected for the sterically unhindered esters of the type of $(ArO)_3P$, $(ArO)_2$.POR, and $(RO)_3P$, etc. in conformity with the formation constants of their complexes with polyvalent metal ions.

A practical rule has been formulated on the basis of the results obtained: for the effective stabilisation of the colour of polymers containing coordination-unsaturated metal ions by vinary organic phosphite—phenolic antioxidant mixtures, it is desirable to introduce the components consecutively: the phosphite is introduced intitially and then the phenolic additive[97].

On the other hand, the chromophoric products of the oxidation of phenolic antioxidants, mainly quinonoid compounds, play a significant role in the appearance of a colour in the stabilisation polymers by phenols[91]. In this case the introduction of organic phosphites also leads to the elimination of colour from the polymer, which is associated with the conversion of the coloured quinonoid compounds into colourless benzene structures.

The reactivity of phosphites in relation to quinones decreases on passing from aliphatic phosphites of the type $(RO)_3P$ (E_a = 22–29 kJ mol^{-1}) to mixed alkyl aryl phosphites $(RO)_2POAr$ and $ROP(OAr)_2$ (E_a = 34–42 kJ mol^{-1}) and further to aromatic phosphites $(ArO)_3P$ (particularly those with an alkyl substituent in the ring)[98].

It is noteworthy that organic phosphites which hardly interact with quinones in model liquid-phase reactions are incapable of weakening appreciably the intensity of the colour of polyolefins even when present in a fourfold excess relative to the concentration of the product of the oxidation of the phenolic antioxidant in the polymer.

Thus new reactions of phosphites, involved in the stabilisation of the colour of complex polymer systems, have been discovered; they involve the chemical binding of the admixtures and the reaction products of the additives introduced. The observed features make it possible to recommend phosphites as synergistic additives for the enhancement of a specific functional activity in devising effective compositions, containing phenolic antioxidants, which do not become coloured.

4. The Stabilising Effects of Phosphite–Phosphite Systems

On the basis of the classification of phosphites in terms of their functional activity under the conditions of the development and branching of degradative processes in polymers, new types of synergistic mixtures have been proposed which make it possible to achieve the effective stabilisation of polymers[99,100]. These mixtures contain phosphites with different types of activity: an inhibitor of radical processes (a sterically hindered aromatic phosphite) and an acceptor of molecular polymer reaction products (aliphatic and mixed alkyl aryl phosphites).

In particular, mixtures of polyphosphite (I), 2,6-di-t-butyl-4-methylphenyl *o*-phenylene phosphite (VII) and 2,2-methylenebis(6-t-butyl-4-methylphenyl) naphthyl phosphite (VIII) with trinaphthyl phosphite proved effective for polyolefins. The mechanism of the stabilising action under these conditions can be explained by the fact that one of the phosphites, for example compound (I), (VII), or (VIII), for which the oxidation chain termination pathway is dominant, accepts the $RO_2^{\cdot}$ radicals, while the other, for example, trinaphthyl phosphite prevents degenerate branching by decomposing hydroperoxides.

This has been demonstrated kinetically by the displacement of the critical concentrations of the corresponding phosphites (free-radical inhibitors) towards lower values in the presence of trinaphthyl phosphite under the conditions of the inhibited oxidation of low-density polyethylene (473 K, 250 mmHg).

The finding that the replacement of trinaphthyl phosphite by dilauryl thiodipropionate (a typical hydroperoxide decomposing agent) and correspondingly of the polyphosphite (I) by 2,2'-methylenebis(6-t-butyl-4-methylphenol) (a typical inhibitor) leads to analogous results conserve as confirmation of the above mechanism. It is of interest that, when a number of phosphite inhibitors are used in compositions with powerful phenolic inhibitors, a synergistic effect is also observed[100]. This shows that, together with the termination of kinetic oxidation chains, such phosphites can also suppress degenerate branching. A particular tendency in their stabilising behaviour is determined by the competitive strength of the compound with synergistic activity.

Thus the elucidation of the complete phenomenological picture of the mechanism of the action of organophosphorus stabilisers, i.e. of the fundamental decisive pathways leading to the stabilisation of polymers by phosphites and systems based on them, permits a well-founded prediction of the structures of phosphites and their compositions most effective as inhibitors of chain initiation and propagation in the ageing process and as colour stabilisers for polymers and of the pathways leading to the enhancement of the key functions of phosphites as stabilisers.

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The Reactivity of Addends in the Diene Synthesis Reaction

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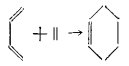
The principal electronic factors determining the reactivity of addends in the diene synthesis reaction are considered. The applicability of the model taking into account both the donor-acceptor properties of the reactants and their relative stabilities with respect to the reaction described by delocalisation energies or reaction enthalpies is demonstrated. The unusual influence of the donor-acceptor interactions between the addends on their selectivity in the Diels-Alder reaction is also demonstrated and the qualitative differences between the effects of the pair interactions of the antisymmetric and symmetrical frontier orbitals are noted.
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I. INTRODUCTION

The diene synthesis reaction (the diene condensation or the Diels–Alder reaction) occupies one of the most important places in modern organic chemistry, constituting a simple and easy method for the synthesis of a wide variety of carbocyclic and heterocyclic systems containing a six-membered fragment:



The range of transformations embraced by the Diels–Alder condensation involves compounds of various types, starting with the simplest olefins and extending up to complex steroid systems[1].

The Diels–Alder reaction is of considerable theoretical interest. The study of its mechanism has been a long process, reflecting the evolution of theoretical views and experimental approaches in organic chemistry. The advances in the understanding of the mechanism of this reaction have been frequently described in reviews devoted to its various aspects[2].

The knowledge of the factors which determine the reactivity of the addends involved in the cycloaddition has played an important role. The study of the Diels–Alder reaction on the basis of non-empirical[3] and semi-empirical[4] quantum-chemical calculations of the potential surfaces of the reactions does not lead at present to unambiguous results[5] and does not permit broad generalisations based on the extensive experimental data obtained in the study of the reactivities of addends of various types. At the same time the approaches employing model ideas, based on the theory of frontier molecular orbitals[6] and on the concept of localisation[7] and permitting the employment of the experimental characteristics of the reactants and reactions for analysis, have already led to the understanding of many features, sometimes unexpected, which control the interaction of the components of the diene condensation. The present review is devoted to the consideration of the results obtained in this field.

II. THE FRONTIER-ORBITAL APPROACH TO THE PROBLEM OF THE REACTIVITY OF ADDENDS

The Diels–Alder reaction, accompanied by a significant loss of degrees of freedom, is characterised by an appreciable decrease of the entropy of the system. As a rule the entropy of reaction is between −30 and −40 e.u.,[8] which implies that the real processes can be only exothermic. Indeed, even for $\Delta H_0 = 0$ (a thermally neutral process), let alone processes with $\Delta H_0 > 0$, the equilibrium constants cannot exceed 10^{-6} for the entropies indicated[9], which corresponds to a virtually complete shift of the equilibrium towards the starting materials. In conformity with Hammond's postulate[10], the transition state in such real diene condensations should be relatively "early" and should be characterised by a low degree of formation of new bonds. Furthermore, diene synthesis is a reaction of components with relatively similar energies of the interacting orbitals. The set of factors indicated not only permits the classification of this reaction as "frontier-orbital-controlled"[11] but also makes it possible to understand why the theory of frontier molecular orbitals can be applied to the reactivity of the addends in its simplest form, developed by a number of investigators[12,13].

According to the approach investigated, a measure of the relative reactivity of a diene–dienophile system is the stabilisation energy of the transition state (ΔE_{st}) determined by the interaction of the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) of the reacting species:

$$\Delta E_{st} = \Delta E^{\text{LUMO dienophile}}_{\text{HOMO diene}} + \Delta E^{\text{LUMO diene}}_{\text{HOMO dienophile}}, \quad (1)$$

$$\Delta E_{st} \cong K[1/(\epsilon_{\text{HOMO diene}} - \epsilon_{\text{LUMO dienophile}}) + 1/(\epsilon_{\text{HOMO dienophile}} - \epsilon_{\text{LUMO diene}})]. \quad (2)$$

According to Eqn.(2),[13] the quantity ΔE_{st} and hence the relative reactivity of the addends ($\lg k \propto \Delta E_{st}$) depend on the difference between the energies ε of the interacting orbitals. The smaller this difference, the higher the reactivity.

Depending on the different relative dispositions of the interacting orbitals of the diene and dienophile, determined by the structure of the addends, there is a possibility of various types of diene synthesis reactions[14] (Fig. 1). The case where the stabilisation energy is determined mainly by the interaction between the HOMO of the diene and the LUMO of the dienophile (the term $\Delta E^{\text{LUMO dienophile}}_{\text{HOMO diene}}$) because $(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}}) < (\varepsilon_{\text{HOMO dienophile}} - \varepsilon_{\text{LUMO diene}})$ corresponds to the "diene (donor) - dienophile (acceptor)" reaction type. An increase of the reactivity of the system following the introduction of electron-donating substituents into the diene and of electron-accepting substituents into the dienophile is characteristic of reactions of this type in conformity with the influence which these substituents exert on the change of the energies of the orbitals.

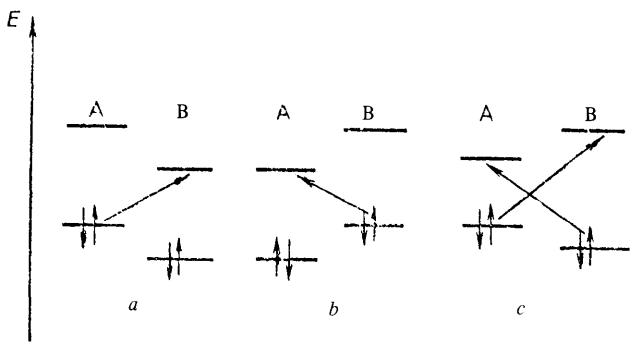


Figure 1. Schematic representation of the relative positions of the frontier orbitals of the addends in the diene synthesis reaction in condensations of the "diene (donor)–dienophile (acceptor)" type (*a*), the "diene (acceptor)–dienophile (donor)" type (*b*), and the "neutral" type (*c*); A = diene; B = dienophile.

Reactions of the "diene (acceptor)–dienophile (donor)" type are characterised by a different relative disposition of the orbitals in the diene and dienophile. In this case the interaction between the HOMO of the dienophile and the LUMO of the diene is decisive because $(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}}) > (\varepsilon_{\text{HOMO dienophile}} - \varepsilon_{\text{LUMO diene}})$. Reaction systems of this type are distinguished by an increase of reactivity following the introduction of electron-accepting substituents into the diene and of electron-donating substituents into the dienophile.

Reactions of these two types were known previously. Thus a theoretical interpretation based on the allowance for the intermolecular donor–acceptor interactions has been achieved for these reactions. However, analysis of the probable situations had led to the conclusion[14] that there is a possibility of the existence of yet another, unknown at the time, type of reaction, called the "neutral" type, where the energies of the pair interactions are comparable: $(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}}) \cong (\varepsilon_{\text{HOMO dienophile}} - \varepsilon_{\text{LUMO diene}})$, whence $\Delta E^{\text{LUMO dienophile}}_{\text{HOMO diene}} \cong \Delta E^{\text{LUMO diene}}_{\text{HOMO dienophile}}$. An increase of the reactivity of the diene–dienophile system should be expected for reactions of this type after the introduction of both electron-donating and electron-accepting substituents into either addend. Subsequent investigations demonstrated the actual existence of reactions of this type (see Section V).

III. REACTIONS OF THE "DIENE (DONOR)–DIENOPHILE (ACCEPTOR)" TYPE

The majority of reactions investigated at the present time belong to this type and one of the first conclusions concerning the electronic nature of the interacting components of diene condensations was that the diene must be an electron donor and the dienophile an electron acceptor[15]. The change in the reactivity of the system as the electronic character of the reactants is altered is consistent with the model considered above.

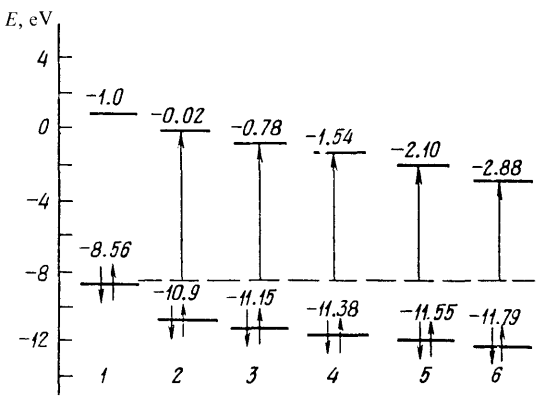


Figure 2. The relative positions of the frontier orbitals of cyclopentadiene (1) and cyanoethylenes: 2) acrylonitrile; 3) maleodinitrile and fumarodinitrile; 4) 1,1-dicyanoethylene; 5) tricyanoethylene; 6) tetracyanoethylene.

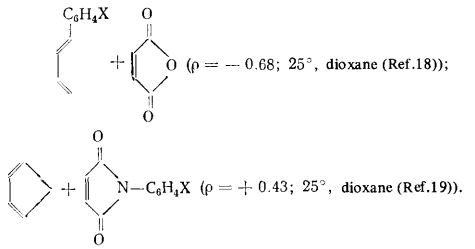
Table 1. The reactivities (k_2, litre mol^{-1} s^{-1}) of cyanoethylenes in the Diels–Alder reactions with cyclopentadiene, 9,10-dimethylanthracene (in dioxane at 20 °C),[13] and 1,3-diphenylisobenzofuran (in dichloroethane at 30 °C).[16]

Dienophile	Cyclopentadiene	9,10-Dimethylanthracene	1,3-Diphenylisobenzofuran
Tetracyanoethylene	480	$1.3\cdot10^{4}$	10^{8}
Tricyanoethylene	4.83	5.88	10^{4}
1,1-Dicyanoethylene	$4.55\cdot10^{-1}$	$1.27\cdot10^{-1}$	$1\cdot10^{3}$
Maleodinitrile	$9.1\cdot10^{-4}$	$1.31\cdot10^{-4}$	1.3
Fumarodinitrile	$8.1\cdot10^{-4}$	$1.39\cdot10^{-4}$	$3.1\cdot10^{-1}$
Acrylonitrile	$1.04\cdot10^{-5}$	$8.9\cdot10^{-7}$	$3.0\cdot10^{-3}$

An example may be provided by the reactions of cyanoethylenes with electron-donating dienes. Table 1 illustrates the influence of the number of CN groups in the dienophile on the reactivity of the system. Fig. 2 illustrates the ratio of the energies of the frontier orbitals of cyclopentadiene and cyanoethylenes[17]. Evidently $(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}}) < (\varepsilon_{\text{HOMO dienophile}} - \varepsilon_{\text{LUMO diene}})$. As the cyano-groups

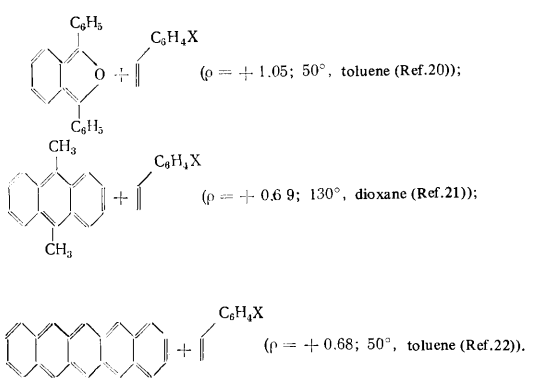
accumulate, the energy gap between the HOMO of cyclopentadiene and the LUMO of cyanoethylene diminishes and the reactivity increases. Thus the reactivity of the dienophile increases with increase of its electron-accepting character (its electron affinity).

The energies of the orbitals change analogously, but on a smaller scale, under the influence of substituents in the aromatic ring of the diene or the dienophile. In this case reactions of the "diene (donor)–dienophile (acceptor)" type should be characterised by reaction constants $\rho > 0$ when the substituents in the dienophile are varied and $\rho < 0$ when the substituents in the diene are varied. This type of phenomenon does indeed occur, for example, in the reactions of arylbutadienes with maleic anhydride and of cyclopentadiene with *N*-arylmaleimides:



In conformity with this, the sign of the reaction constants indicates a specific type of reaction and its low absolute value points to a synchronous reaction mechanism. Correlation data are now available for more than 10 reaction series of the "diene (donor) - dienophile (acceptor)" type and some of them have been listed[2].

It is of interest to examine reactions with participation of styrenes as dienophiles. These compounds provide a kind of test for the type of reaction, determined by the electronic character of the diene. Data concerning reactions involving certain electron-donating dienes are presented below:



In the last case an estimate of the frontier orbital energies shows (Fig.3*a* presents data concerning pentacene and unsubstituted styrene) that the system should be close to the "neutral type" if not actually of this type (the study was performed in order to detect "neutral" reactions). Nevertheless, a reaction of the "diene (donor)–dienophile (acceptor)" is observed. The possible causes of this phenomenon will be discussed below.

It is noteworthy that the influence of the substituents in the diene is described by the electrophilic constants σ^+; the influence of substituents in the dienophiles containing, apart from these substituents, other groups capable of direct polar conjugation with the +C reaction centre, is described by the Hammett constants σ, while the influence of substituents in styrenes is described by the nucleophilic constants σ^-.

Not all the reaction series obey rigorously the correlations (Table 2) but here too a tendency towards an increase of the reactivity of the system was observed as the electron-donating properties of the diene and the electron-accepting properties of the dienophile are enhanced.

Table 2. The reactivities (k_2, litre mol^{-1} s^{-1}) of acenes in the diene synthesis reactions with *N*-(X-phenyl)maleimides in toluene at 60 °C,[23,24] the ionisation potentials (I_D) of the acenes, and the electron affinities (E_A) of the dienophiles[23,24].

Diene	I_D, eV	X				
		p-$(CH_3)_2N$	*p*-CH_3O	H	*p*-Br	*p*-NO_2
Pentacene	6.64	0.42	0.62	0.75	1.49	3.36
6,13-Dichloropentacene	6.63	$4.30\cdot10^{-2}$	$5.80\cdot10^{-2}$	$5.70\cdot10^{-2}$	$1.00\cdot10^{-1}$	$1.80\cdot10^{-1}$
Tetracene	7.01	$1.65\cdot10^{-2}$	$2.22\cdot10^{-2}$	$2.45\cdot10^{-2}$	$4.62\cdot10^{-2}$	$9.65\cdot10^{-2}$
5,11-Dichlorotetracene	6.81	$3.30\cdot10^{-3}$	$4.00\cdot10^{-3}$	$4.10\cdot10^{-3}$	$7.70\cdot10^{-3}$	$1.16\cdot10^{-2}$
Anthracene	7.40	$1.91\cdot10^{-4}$	$2.46\cdot10^{-4}$	$2.78\cdot10^{-4}$	$4.28\cdot10^{-4}$	$5.79\cdot10^{-4}$
E_A, eV		0.7	0.9	0.9	0.95	1.0

Table 3. The reactivities (k_2, litre mol^{-1} s^{-1}) of substituted butadienes in the Diels–Alder reactions with maleic anhydride (dioxane, 30 °C), tetracyanoethylene (dioxane, 20 °C), and 4-phenyl-1,2,4-triazoline-3,5-dione (benzene, 25 °C) [26,27] and the ionisation potentials (I_D) of the dienes.

Diene	I_D, eV	PTAD	MA	ТЦЭ
2,3-Dimethylbuta-1,3-diene	8.76	183	$3.36\cdot10^{-4}$	$2.43\cdot10^{-1}$
trans-1-Phenylbuta-1,3-diene	8.16	63	$1.12\cdot10^{-4}$	$6.68\cdot10^{-2}$
2-Methylbuta-1,3-diene	9.04	46	$1.54\cdot10^{-4}$	$1.13\cdot10^{-2}$
Buta-1,3-diene	9.07	6.9	$6.83\cdot10^{-5}$	$5.19\cdot10^{-3}$
trans,trans-1,4-Diphenylbutadiene	7.54	5.1	$2.96\cdot10^{-6}$	$8.4\cdot10^{-3}$

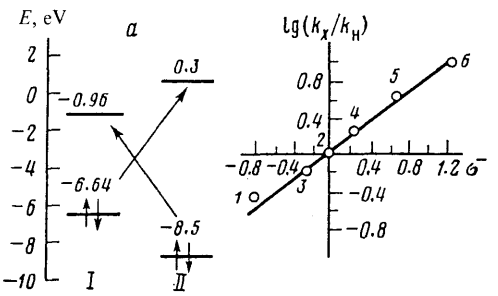


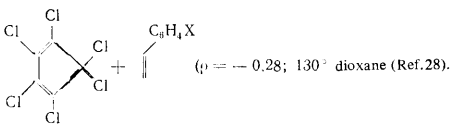
Figure 3. *a*) The relative positions of the frontier orbitals of pentacene (I) and styrene (II); *b*) dependence of the relative reactivities of styrenes [$\lg(k_X/k_H)$] in the diene synthesis reaction with pentacene on the nucleophilic constants of the substituents (toluene, 60 °C). Substituents X in styrenes: 1) *p*-$(CH_3)_2N$; 2) H; 3) *p*-CH_3O; 4) *p*-Br; 5) *m*-NO_2; 6) *p*-NO_2; $\rho = 0.685$; $r = 0.992$.

Finally, one should point out the existence of reaction series in which the variation of the reactivity of the system for a series of related compounds is inconsistent with the variation of the electronic character of the reactant, although there is no doubt about the assignment to a particular type

of reaction [in the given instance to the "diene (donor)–dienophile (acceptor)" type]. Table 3 presents data referring to the reactions of a series of butadienes with tetracyanoethylene (TCE), maleic anhydride (MA), and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). Evidently phenylated butadienes have a reduced reactivity compared with that expected on the basis of their electron-donating properties. The reactivity series of substituted butadienes are found to be different in reactions with different dienophiles. The possible causes of this phenomenon will be examined below (in Section VII).

IV. REACTIONS OF THE "DIENE (ACCEPTOR)–DIENOPHILE (DONOR)" TYPE

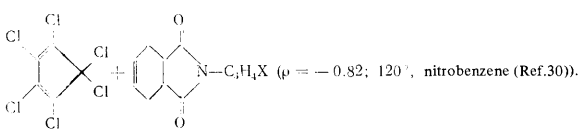
The existence of reactions of this type was first demonstrated as a result of a kinetic study of the reactions of hexachlorocyclopentadiene with styrenes:



($\rho = -0.28$; 130° dioxane (Ref.28).

A conclusion concerning the type of reaction was reached on the basis of the sign of the reaction constant. Examination of the ratio of the energies of the frontier orbitals (Fig.4) confirms that this conclusion is well founded. The stabilisation of the transition state in the given system is due to the preferential interaction of the HOMO of the dienophile with the LUMO of the diene.

Hexachlorocyclopentadiene reacts as an electron-accepting diene also with dienophiles such as the *N*-arylimides of *cis*-4-cyclohexene-1,2-dicarboxylic acid and *N*-arylimides of *endo*- and *exo*-bicyclo[2.2.1]heptene-2,3-dicarboxylic acid[29,30], for example:



($\rho = -0.82$; 120°, nitrobenzene (Ref.30)).

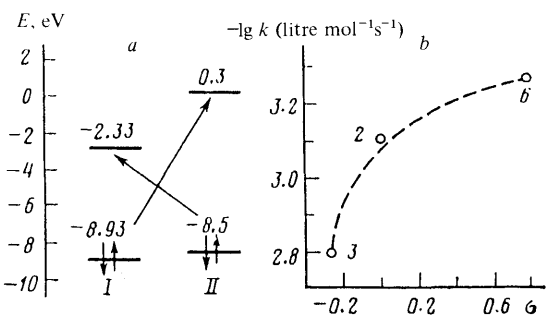
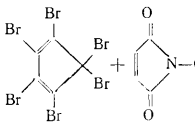


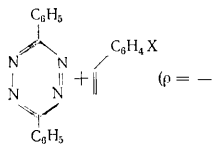
Figure 4. *a*) The relative positions of the frontier orbitals of hexachlorocyclopentadiene (I) and styrene (II); *b*) dependence of the reactivities of styrenes ($\lg k$) in the diene synthesis reaction with hexachlorocyclopentadiene on the Hammett σ constants (dioxane, 130 °C). The numbers of the styrenes correspond to the numbers of the compounds in Fig.3*b*.

It is of interest that the reactions of hexabromocyclopentadiene are of the "diene (acceptor)–dienophile (donor)" type even with electron-accepting dienophiles such as *N*-arylmaleimides:

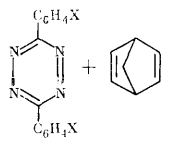


($\rho = -0.28$; 80°, benzene (Ref.31)).

Substituted tetrazines also behave as electron-accepting dienes. The influence of substituents in both the diene and the dienophile has been traced in relation to these compounds:



($\rho = -0.59$; 120°, nitrobenzene (Ref.2));



($\rho = +1.25$; 30°, dioxane (Ref.2)).

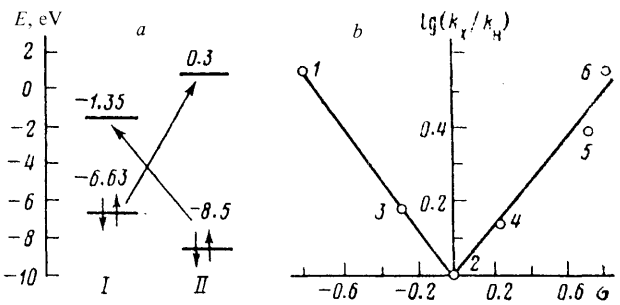


Figure 5. *a*) The relative positions of the frontier orbitals of 6,13-dichloropentacene (I) and styrene (II); *b*) dependence of the relative reactivities of styrenes in the diene synthesis reaction with 6,13-dichloropentacene on the Hammett σ constants (toluene, 50 °C). The numbers of the styrenes correspond to the numbers of the compounds in Fig.3*b*.

V. REACTIONS OF THE "NEUTRAL" TYPE

The experimental evidence for the occurrence of reactions of the "neutral" type was first obtained in the study of the interaction of cyclones (phencyclone, tetracyclone, and acecyclone) with styrenes and arylacetylenes[32–35]. According to Sustmann[14], when the arrangement of the frontier orbitals in the addends is nearly symmetrical (the neutrality condition), both electron-donating and electron-accepting substituents increase ΔE_{st} and hence should increase the reactivity of the system; thus the dependence of $\lg k$ on the σ constants of the substituents should be U-shaped. However, for a symmetrical disposition of the frontier orbitals, the differences between the energies of the HOMO and LUMO of the addends may be large and the reactivity of the system is therefore small. For this reason, the closeness of the orbitals in one of the addends must be adopted as the condition for

the occurrence of such reactions (the condition for reactivity). It is more likely that the levels are close to one another in dienes, which are usually more conjugated. Cyclones, which are intensely coloured, satisfy this condition. The "neutral" character of the reactions of cyclones with styrenes has been confirmed in recent studies[36].

The dienes which react with styrenes via a "neutral" mechanism proved to be also 6,13-dichloropentacene, 5,11-dichlorotetracene, and tetrachloro- and tetrabromo-*o*-quinones[25,37,38].

From data for the orbital characteristics of the reactants, it was initially postulated that, among polynuclear hydrocarbons, the diene capable of undergoing "neutral" reactions with styrenes may be pentacene. However, it was found that in this instance a reaction of the "diene (donor)–dienophile (acceptor)" type takes place (see Section III). After the introduction of chlorine atoms in the *meso*-positions (6,13-positions), i.e. after imparting electron-accepting properties to the diene, the "neutral" type of reaction can be observed (Fig.5).

Fig.6*a* presents estimates of the energies of the tetrachloro-*o*-quinone–styrene orbital system, which show that in this case the diene should be an electron acceptor relative to the dienophile; therefore, in formulating these experiments, reactions of the "diene (acceptor)–dienophile (donor)" type were expected. However, it was found that in this case reactions of the "neutral" type actually occur with inversion at the halogen as the substituent in the styrene molecule (Fig.6*b*).

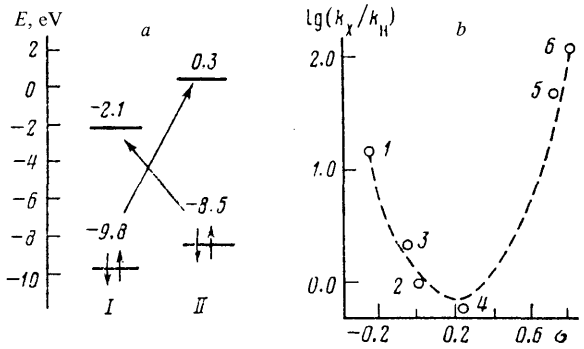
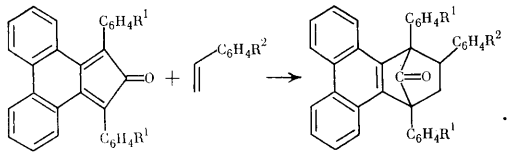


Figure 6. *a*) The relative positions of the frontier orbitals of tetrachloro-*o*-benzoquinone (I) and styrene (II); *b*) dependence of the relative reactivities of styrenes [lg (k_X/k_H)] in the diene synthesis reaction with tetrachloro-*o*-benzoquinone on the Hammett σ constants (dichloroethane, 30 °C). Substituents X in styrenes: 1) *p*-CH_3O; 2) H; 3) *m*-CH_3; 4) *p*-Cl; 5) *m*-NO_2; 6) *p*-NO_2.

A characteristic feature of all the reactions of the "neutral" type investigated is that the diene in these substances is to some extent an electron acceptor relative to the dienophile.

There exist data clearly demonstrating the possibility of transitions between the various types of reactions. Such transitions can be observed within narrow cross reaction series and more effectively when there is a sharp change in the electronic character of the reactants. An example of a transition of the first kind is provided by the change in the reactivity of substituted phencyclones in the Diels–Alder reactions with styrenes[39] (Table 4):



The variation of the reactivity of styrenes in reactions with various cyclones (Table 4) corresponds in all cases to the "neutral" type of reaction, but, on passing from the phencyclone containing the electron-accepting *p*-NO_2 substituents to the phencyclone with electron-donating *p*-CH_3O substituents, the reactivity of styrenes with electron-donating substituents diminishes and that of styrenes with electron-accepting substituents increases with inversion in the region of *p*-bromostyrene.

Table 4. The reactivities (10^3 k_2, litre mol^{-1} s^{-1}) of substituted phencyclones in the Diels–Alder reactions with styrenes (toluene, 40 °C).[39]

R^2	R^1					ρ
	p-NO_2	*p*-Cl	H	*p*-CH_3	*p*-CH_3O	
p-NO_2	6.12	11.7	18.2	22.0	23.2	−0.575
m-NO_2	4.52	7.00	7.90	11.2	9.30	−0.342
p-Br	8.15	8.70	7.50	9.45	7.40	0.008
H	9.40	6.00	4.40	4.10	4.60	0.339
p-CH_3O	40.1	18.5	12.4	13.3	12.0	0.511
p-$(CH_3)_2N$	710	112	74.8	45.5	54.8	1.124

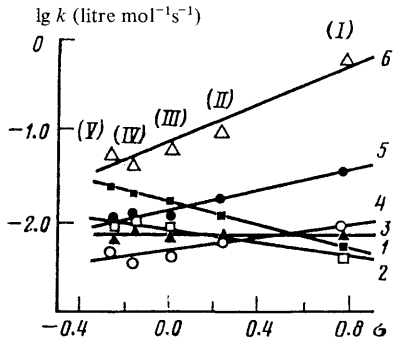


Figure 7. Dependence of the reactivities of the substituted phencyclones (I)–(V) in the diene synthesis reaction with styrenes (lines *1*–*6*) on the Hammett σ constants (toluene, 40 °C). Substituents R^1 in phencyclones: I) *p*-NO_2; II) *p*-Cl; III) H; IV) *p*-CH_3; V) *p*-CH_3O. Substituents R^2 in styrenes: 1) *p*-NO_2; 2) *m*-NI_2; 3) *p*-Br; 4) H; 5) *p*-CH_3O; 6) *p*-$(CH_3)_2N$.

The reactivity of cyclones varies somewhat differently in reactions with different styrenes (Table 4 and Fig.7). The reactions of cyclones with *p*-nitrostyrene are of the "diene (donor)–dienophile (acceptor)" type and the type of reactions remains unchanged but the reactivity and selectivity of the

reactants diminish. The reactions with *p*-bromostyrene are almost insensitive to the influence of the substituents in cyclones[13,14]. The reactions with unsubstituted styrene, *p*-methoxystyrene, and *p*-dimethylaminostyrene are of the "diene (acceptor)–dienophile (donor)" type. In the series of styrenes considered there is an increase of not only the reactivity but also of the selectivity of the reactants. As it were, "macroneutrality" is obtained, i.e. a transition from reactions of one type to another in a number of reaction series, in contrast to the "microneutrality" observed within the limits of a single reaction series.

A transition from reactions of one type to another has also been demonstrated for wider variations of dienes and dienophiles. The change in the type of reaction after the introduction of halogen atoms into the pentacene molecule has already been demonstrated (see Sections III and V); other examples also exist. Thus the reactions of indanocyclones, which have more pronounced electron-accepting properties than phencyclones, tetracyclones, and acecyclones, with styrenes are of the "diene (acceptor)–dienophile (donor)" type[40]; on the other hand, the reactions of cyclones with *N*-arylmaleimides and maleic anhydride–dienophiles with more pronounced electron-accepting properties than styrenes—are of the "diene (donor)–dienophile (acceptor)" type[41,42]. Reactions of an analogous type are observed in systems comprising phencylone and vinyl and isopropenyl dienophiles with electron-accepting substituents[43]. Hexabromocyclopentadiene (Section IV) and tetrabromo-5,5-dimethoxycyclopentadiene react with *N*-arylmaleimides in different ways. In the latter case the reaction of the "diene (donor)–dienophile (acceptor)" type is observed[31].

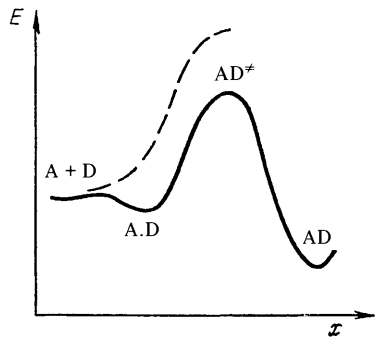


Figure 8. Schematic representation of the energy profile of the diene synthesis reaction proceeding via a charge-transfer complex stage; x = reaction coordinate.

Thus the above discussion demonstrates the applicability of the model based on the frontier-orbital aproach and indicates a significant influence of intermolecular orbital donor–acceptor interactions on the reactivity of diene–dienophile systems.

It is noteworthy that the donor–acceptor interactions between the addends involved in the diene synthesis have already attracted the attention of investigators for a long time. One of the signs of such interactions is the formation of complexes between the diene and the dienophile[44–49], which should be classified as charge-transfer complexes of the π,π-type according to the existing views[50].

The existing data for the relation between the donor–acceptor properties of the addends and the stability of the complexes which they form and the reactivity[51–53], data for the influence of solvents on the diene synthesis and complex formation[54–57], and the characteristic features of the kinetics of certain reactions with a negative temperature coefficient[58] permitted the conclusion that the charge-transfer complexes (CTC) formed between the addends arise in the course of the diene synthesis and are thus prereaction complexes[59]. Donor–acceptor interactions lead to the stabilisation of the system and to a decrease of the potential energy over the entire initial reaction pathway, including the prereaction stage (Fig.8). In this sense the CTC between the addends are prereaction complexes not only as regards their position in the chain of transformations but also as regards their physical nature, while the donor–acceptor interactions are one of the factors determining the reactivity of the system[60]. The formation of the CTC and their characteristics can serve as an indication of the manifestation and intensity of donor–acceptor interactions. According to Markov[61], the elucidation of the role of the CTC is an experimental prerequisite of the application of theoretical approaches based on the consideration of intermolecular orbital donor–acceptor interactions.

One should note that the following scheme is usually postulated for the energy profile of the reaction involving the formation of CTC during diene synthesis:

$$A + D \overset{K}{\rightleftarrows} A.D \overset{k_1}{\rightarrow} AD,$$

where A and D are the free addends (the acceptor and the donor), A.D is the complex, and AD is the adduct. This scheme presupposes that the adduct is formed only from the CTC and that the rate of reaction is proportional to its concentration [A.D]:

$$w = k_1[A \cdot D] = Kk_1[A] \cdot [D]. \qquad (3)$$

According to this scheme and Eqn.(3), on passing from systems forming complexes to those where complexes are not produced, the possibility of the reaction is eliminated ($k_{exp} = Kk_1 \to 0$, since $K \to 0$); however, this conflicts with what is observed in reality.

It is more correct to suppose[59] that in the case of systems with CTC the adduct is formed both from the complex A.D and directly from the free addend A and D. The reaction complex, following the same energy profile of the reaction, then proceeds via the CTC state but without a kinetically independent species being detected.

Overall we have a scheme according to which the addends in the initial state are divided, in accordance with the equilibrium constant, into bound (A.D.) and free (A and D). The adduct is formed from both[15,16]:

$$\begin{array}{ccccc} A + D & \overset{K}{\rightleftarrows} & A.D & \overset{k_1}{\rightarrow} & AD \\ \uparrow & & & & \uparrow \\ \multicolumn{5}{c}{\underline{\qquad\qquad k_2 \qquad\qquad}} \end{array}$$

The rate of the process is then described by the expression

$$w = k_1[A.D] + k_2[A][D] = (Kk_1 + k_2)[A][D]$$

and the quantity

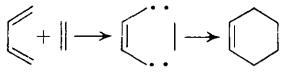
$$k_{exp} = (Kk_1 + k_2) \to k_2 \text{ when } K \to 0$$

corresponds to the transition to systems without CTC mentioned above.

VI. DELOCALISATION ENERGIES. THERMOCHEMISTRY OF THE REACTIONS

The formation of the cycloadduct entails changes in the initial π-electron systems of the diene and dienophile, which correspond to the localisation of two π electrons in the 1,4-positions in the diene and two π electrons in the 1,2-positions

in the dienophile. The corresponding changes in the π-electron energy can be regarded as the 1,4-delocalisation (for the diene) and 1,2-delocalisation (for the dienophile) energies[7]:



Delocalisation is an endothermic process and the differences between the delocalisation energies of dienes and dienophiles characterises the difference between the stabilities of the reactants due to the delocalisation of the electrons. The concept of delocalisation was introduced by Brown[62] ("para-localisation" for polynuclear hydrocarbons as dienes) as the index of the reactivity of these compounds in diene synthesis on the grounds that compounds with a lower delocalisation energy should form more stable (as regards retrodecomposition) adducts, so that these compounds should be more reactive in conformity with the Bell–Evans–Polanyi principle.

The relation between the enthalpy of reaction (stability of the adducts) and the delocalisation energy is illustrated in Fig. 9,[60] according to which the enthalpy of reaction is determined mainly by the delocalisation energies ($L_{1,4}$ and $L_{1,2}$) and also by the energies of formation of new bonds and the energy of rehybridisation in the delocalised states ($E_\sigma + E_S$). If it is assumed that, in a reaction series with the same diene (or dienophile), the 1,4-delocalisation (or 1,2-delocalisation) energy, the energy of formation of new bonds, and the rehybridisation energy are constant, then the differences between the enthalpies of reaction should be determined by the differences between the 1,2-delocalisation (or 1,4-delocalisation) energies. The enthalpy of reaction in a given reaction series can then serve as a measure of the delocalisation energy.

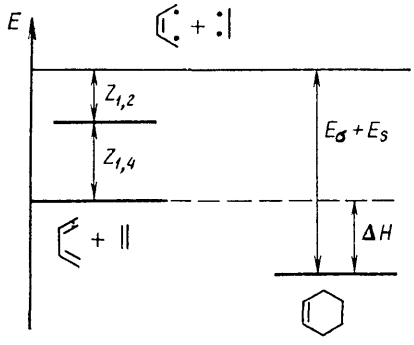


Figure 9. Schematic representation of the relation between the enthalpies of the diene synthesis reaction ΔH and delocalisation energies (for explanation, see text).

Until recently there were almost no literature data for the enthalpies of reaction. They were known for certain reversible reactions because they were determined from the temperature variation of the equilibrium constant[8]. As microcalorimetric methods have developed, the situation has changed, but reliable determinations of such quantities are so far restricted to rapid processes with a very reactive addend as at least one of the components; in particular, tetracyanoethylene and 1,3-diphenylisobenzofuran are used as the dienophile and the diene respectively (Tables 5 and 6).

Table 5. The enthalpies of the reactions[10,64] of various dienes with tetracyanoethylene at 25 °C, the increments in the enthalpies of reaction for the dienes (Δh_{IBF}),[63,64] and the ionisation potentials of the dienes.

Diene	I_D, eV	$-\Delta H$, kcal mol^{-1}	Δh_{IBF}, kcal mol^{-1}
9,10-Dimethylanthracene	7.23	21.1	—4.6
9-Methylanthracene	7.26	20.2	—5.8
Anthracene	7.47	18.5	—2.0
9-Chloroanthracene	7.45	15.3	0.7
9-Methoxyanthracene	7.20	14.6	1.9
9,10-Dimethoxyanthracene	7.09	12.6	3.9
Tetracene	7.01	23.1	—6.6
Pentacene	6.64	27.7	—11.2
5,11-Dichlorotetracene	6.81	18.7	—2.2
6,13-Dichloropentacene	6.63	17.7	—1.2
Buta-1,3-diene	9.03	36.8	—20.3
2-Methylbuta-1,3-diene	8.89	39.7	—23.2
2-Methoxybuta-1,3-diene	8.62	37.9	—21.4
2,3-Dimethylbuta-1,3-diene	8.62	42.0	—25.5
trans-Penta-1,3-diene	8.61	39.0	—22.5
trans-1-Phenylbuta-1,3-diene	8.16	34.0	—17.5
trans, trans-1,4-Diphenylbuta-1,3-diene	8.09	23.2	—6.7
Cyclohexa-1,3-diene	8.25	31.0	—14.5
Cyclopenta-1,3-diene	8.58	26.9	—10.4
1,3-Diphenylisobenzofuran	7.62	16.5	0

Table 6. The enthalpies of the reactions of various dienophiles with 1,3-diphenylisobenzofuran at 25 °C, the increments of the enthalpies of reaction for these dienophiles (Δh_{TCE}),[16,65] and the electron affinities of the dienophiles.

Dienophile	$-\Delta H$, kcal mol^{-1}	Δh_{TCE}, kcal mol^{-1}	E_A, eV
Tetracyanoethylene	16.5	0	2.88
Tricyanoethylene	17.0	—0.5	2.10
1,1-Dicyanoethylene	18.4	—1.9	1.53
Maleodinitrile	20.0	—3.5	0.78
Fumarodinitrile	19.7	—3.2	0.78
Acrylonitrile	20.9	—4.4	0.02
Maleic anhydride	20.4	—3.9	0.97
N-(*p*-Nitrophenyl)maleimide	23.0	—6.5	1.01
N-Phenylmaleimide	23.5	—7.0	0.89
N-(*p*-Dimethylaminophenyl)maleimide	23.9	—7.4	0.79
4-Phenyl-1,2,4-triazoline-3,5-dione	25.0	—8.5	1.80
p-Benzoquinone	15.7	0.8	—
1,4-Naphthoquinone	13.8	2.7	—
Acrolein	18.1	—1.6	—
Acrylic acid	20.1	—3.6	—
Methyl acrylate	20.2	—3.7	—
Methacrolein	14.9	1.6	—
Methacrylic acid	15.9	0.6	—
Methyl methacrylate	16.6	—0.1	—
Methacrylonitrile	17.5	—1.0	—

Analysis of the existing data[63] shows that the enthalpies of the reactions of substituted anthracenes are satisfactorily correlated with the 1,4-delocalisation energies calculated for these reactions (Fig. 10). An analogous correlation has been observed also in a series of dienophiles, as shown in relation to cyanoethylene[16], the difference between the enthalpies of the reactions of tetracyanoethylene and acrylonitrile (4.5 kcal mol^{-1}) corresponding to the difference between the calculated delocalisation energies (4.4 kcal mol^{-1} [63]). The difference between the enthalpies of the reactions of anthracene and tetracene, amounting to 4.65 kcal mol^{-1}, also agrees with the calculated value of 5.5 kcal mol^{-1}.[7] In addition, correlations have been observed between the enthalpies of reactions involving the same compounds in different reaction series. Fig. 11 illustrates the relation between the enthalpies of the reactions of a series of dienes with tetracyanoethylene and 4-phenyl-1,2,4-triazoline-3,5-dione. The slope of the straight line in Fig. 11 is 1.0. These data show that the difference between the enthalpies of the reactions of dienes depends insignificantly if at all on the nature of the dienophile, i.e. are determined mainly by the properties of the diene. On the

other hand, the enthalpies of the reactions of a single dienophile can also differ from those for another dienophile, regardless of the nature of the diene, the difference being fairly constant. Fig.12 confirms this conclusion for other pairs of reactions. Furthermore, such differences are maintained in reactions of different kinds: for (4 + 2)- and (3 + 2)-cycloaddition or (4 + 2)- and (2 + 2)-cycloaddition[67,68].

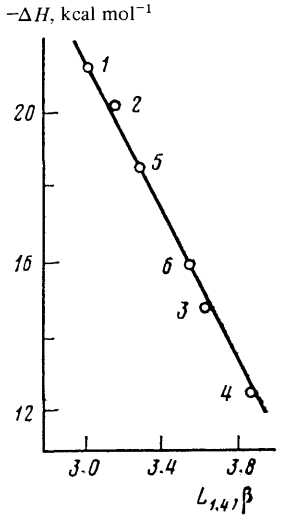


Figure 10. Dependence of the 1,4-localisation energies of substituted anthracene on the enthalpies of the reaction of these dienes with tetracyanoethylene: 1) 9,10-dimethylanthracene; 2) 9-methylanthracene; 3) 9-methoxyanthracene; 4) 9,10-dimethoxyanthracene; 5) anthracene; 6) 9-chloroanthracene; $r = 0.995$.

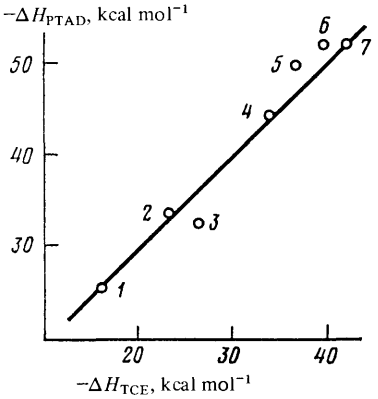


Figure 11. Relation between the enthalpies of the diene synthesis reactions of 4-phenyl-1,2,4-triazoline-3,5-dione (ΔH_{PTAD}) and tetracyanoethylene (ΔH_{TCE}) with various dienes: 1) 1,3-diphenylisobenzofuran; 2) *trans,trans*-1,4-diphenylbuta-2-diene; 3) cyclopentadiene; 4) *trans*-1-phenylbutadiene; 5) butadiene; 6) 2-methylbutadiene; 7) 2,3-dimethylbutadiene.

The results obtained (for a detailed analysis and a broad generalisation, the studies in this field should undoubtedly be continued) already justify the assumption that the differences between the enthalpies of the reactions reflect primarily the difference between the delocalisation energies of the addends, although they also represent an accumulation of other effects, including, for example, the energy of the *s-trans–s-cis* transition in the case of butadienes, etc. This conclusion is important for the understanding of the nature of the phenomenon, bearing in mind the subsequent application of these quantities (Section VII). The "transferability of the differences" makes it possible to estimate the enthalpies of the reactions which cannot be obtained or which have not so far been obtained by direct experimental determinations.

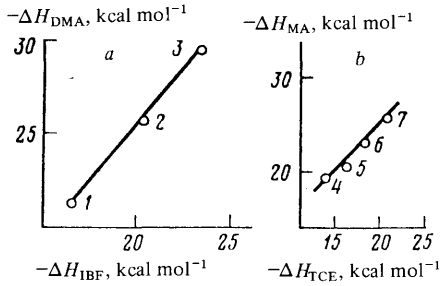


Figure 12. Relations between the enthalpies of the diene synthesis reactions of 9,10-dimethylanthracene (DMA) and 1,3-diphenylisobenzofuran (IBF) with various dienophiles (*a*) and of maleic anhydride (MA) and tetracyanoethylene (TCE) with various dienes (*b*): 1) tetracyanoethylene; 2) maleic anhydride; 3) *N*-phenylmaleimide; 4) 9-methoxyanthracene; 5) 1,3-diphenylisobenzofuran; 6) anthracene; 7) 9,10-dimethylanthracene.

Table 7. The enthalpies of the diene synthesis reactions involving various dienophiles at 25 °C.[64,65]

No.	Diene	Dienophile	$-\Delta H$, kcal mol^{-1}
1	Buta-1,3-diene	PTAD	49.8
2	2-Methylbuta-1,3-diene	PTAD	52.0
3	2,3-Dimethylbuta-1,3-diene	PTAD	52.1
4	*trans*-1-Phenylbuta-1,3-diene	PTAD	44.4
5	*trans, trans*-1,4-Diphenylbuta-1,3-diene	PTAD	33.8
6	Cyclopentadiene	PTAD	32.1
7	Hexachlorocyclopentadiene	PTAD	18.4
8	Hexabromocyclopentadiene	PTAD	15.3
9	Tetrabromo-5,5-dimethoxycyclopentadiene	PTAD	23.1
10	9,10-Dimethylanthracene	MA	25.7
11	Anthracene	MA	23.2
12	9-Methoxyanthracene	MA	19.1
13	9,10-Dimethylanthracene	PMI*	29.4

*N-Phenylmaleimide.

For this purpose, at the present stage of the investigation, having adopted the reaction of tetracyanoethylene with 1,3-diphenylisobenzofuran as the standard, we have listed in Tables 5 and 6 the increments in the enthalpies of the reactions of dienes (Δh_{IBF}) and dienophiles (Δh_{TCE}) which represent the differences between the enthalpies of the reaction of the given diene with tetracyanoethylene or of the given dienophile with 1,3-diphenylisobenzofuran and the enthalpy of the standard reaction [between 1,3-diphenylisobenzofuran (IBF) and tetracyanoethylene (TCE)]. These quantities characterise respectively the relative stabilities of the adducts in the series of dienes and dienophiles considered here. The calculated enthalpy of the reaction of a

given diene (A) and a given dienophile (B) is then equal to the sum of their increments and the enthalpy of the reaction between the tetracyanoethylene and isobenzofuran (−16.5 kcal mol^{-1}):

$$\Delta H^{A+B}\ (\text{kcal mol}^{-1}) = \Delta h^{A}_{IBF} + \Delta h^{B}_{TCE} - 16.5.$$

Comparison of the quantities calculated in this way and the experimental values (Table 7) is illustrated in Fig. 13.

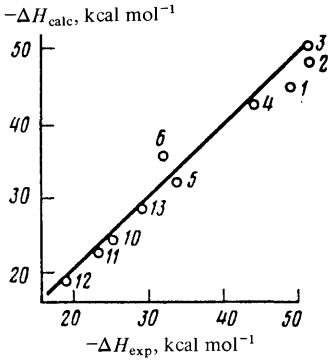


Figure 13. Relation between the experimental (ΔH_{exp}) and calculated (ΔH_{calc}) enthalpies of the diene synthesis reactions; the numbers against the circles correspond to the data in Table 7.

Certain enthalpies of the reactions of dienes, in particular hexachloro- and hexabromo-cyclopentadienes, with tetracyanoethylene have also been estimated from the data obtained. The calculated values are −9.9 and −6.8 kcal mol^{-1} respectively and show that the equilibrium in these reactions should be fully displaced towards the starting materials, i.e. reaction is virtually impossible. This explains the failure of the attempts to obtain the adducts of tetracyanoethylene with the above dienes[69]: it is not the low reactivity of the system but the position of the equilibrium which is responsible for the above phenomenon and, instead of being improved, the situation is actually aggravated by carrying out the reaction at high temperatures. It is indeed known, for example, that the reactions of tetracyanoethylene with 9-chloro-, 9-methoxy-, and 9,10-dimethoxy-anthracenes are reversible[70,71]. In the last instance the equilibrium is almost completely displaced towards the starting materials†. This justifies the assumption that the reactions with $\Delta H \geqslant -15$ kcal mol^{-1} should be reversible while the reactions with $\Delta H \geqslant -12$ kcal mol^{-1} cannot be achieved under the usual conditions.

It is also noteworthy that, according to Tables 6 and 7, in a series of dienophiles belonging to the same reaction series (cyanoethylenes, arylmaleimides, and vinyl and isopropenyl compounds), less stable adducts correspond to more reactive dienophiles in reactions of the "diene (donor)–dienophile (acceptor)" type, in conformity with the hypothesis put forward previously on the basis of model quantum-chemical calculations[60]. This is why the attempts to employ tetracyanoethylene as the competing "displacing" reagent in certain reversible reactions have been unsuccessful[70]. The choice based on the principle of the "reactivity" of the reagent led to an unstable adduct.

† The enthalpy of reaction was determined from data for the retrodecomposition of the adduct by a special method[63].

VII. THE REACTIVITY OF DIENE–DIENOPHILE SYSTEMS

After the qualitative establishment of the fact that the addends in the diene synthesis are of different electronic character, attempts were made to observe correlations between the reactivity of the dienes and dienophiles, on the one hand, and their donor–acceptor characteristics (ionisation potentials and electron affinities), on the other, in order to elucidate the role of the donor–acceptor interactions between the addends reflected in the formation of CTC. It has been shown[16,51,52,60] that such correlations are observed but only within the limits of narrow reaction series. Naturally, the influence of the constant reactant is not then taken into account.

Nevertheless, the model of the interaction of frontier molecular orbitals described in Section II provides a basis for the consideration of the reactivities of diene–dienophile systems with simultaneous allowance for both the electron-donating properties of one addend and the electron-accepting properties of the other. Thus, according to Section II, $\Delta E_{st} \propto$

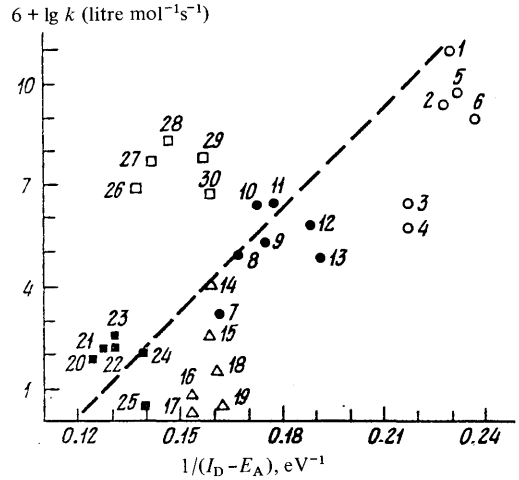


Figure 14. Dependence of the lg k on $1/(I_D - E_A)$ for different diene–dienophile systems. Reactions of tetracyanoethylene with anthracenes: 1) 9,10-dimethylanthracene; 2) 9-methylanthracene; 3) anthracene; 4) 9-chloroanthracene; 5) 9-methoxyanthracene; 6) 9,10-dimethoxyanthracene (dichloroethane, 25 °C [63]). Reactions of tetracyanoethylene with butadienes: 7) buta-1,3-diene; 8) 2-methylbuta-1,3-diene; 9) *trans*-1-methylbuta-1,3-diene; 10) 2,3-dimethylbuta-1,3-diene; 11) 2-methoxybuta-1,3-diene; 12) *trans*-1-phenylbuta-1,3-diene; 13) *trans,trans*-1,4-diphenylbuta-1,3-diene (methylene chloride, 20 °C [74]). Reactions of maleic anhydride with anthracenes: 14) 9,10-dimethylanthracene; 15) 9-methylanthracene; 16) anthracene; 17) 9-chloroanthracene; 18) 9-methoxyanthracene; 19) 9,10-dimethoxyanthracene (dioxane, 30 °C [73]). Reactions of maleic anhydride with butadienes: 20) buta-1,3-diene; 21) 2-methylbuta-1,3-diene; 22) *trans*-1-methylbuta-1,3-diene; 23) 2,3-dimethylbuta-1,3-diene; 24) *trans*-1-phenylbuta-1,3-diene; 25) *trans,trans*-1,3-diphenylbuta-1,3-diene (dioxane, 30 °C [74]). Reactions of 4-phenyl-1,2,4-triazoline-3,5-dione with butadienes; 26) buta-1,3-diene; 27) 2-methylbuta-1,3-diene; 28) 2,3-dimethylbuta-1,3-diene; 29) *trans*-1-phenylbuta-1,3-diene; 30) *trans,trans*-1,4-diphenylbuta-1,3-diene (benzene 25 °C [27]).

$1/(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}})$ for reactions of the "diene (donor)–dienophile (acceptor)" type and, since $\lg k \propto \Delta E_{st}$, it follows that $\lg k \propto 1/(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}})$; or, using experimental quantities, namely the ionisation potential I of the electron-donating diene and the electron affinity E_A of the electron-accepting dienophile, $\lg k \propto 1/(I_D - E_A)$.[12,17,72] Comparison of the reactivities of certain diene–dienophile systems with the reciprocals of the differences between the ionisation potentials of the dienes and the electron affinities of the dienophiles shows that in this instance the correlations are limited to individual reaction series[17,72,73] or are not observed at all[74].

The set of data referring to different diene–dienophile systems which can be considered from the above standpoint and discussed further is presented in Figs. 14 and 15#. Evidently, although a definite tendency towards an increase of the reactivity of diene–dienophile systems with decrease of the difference between the ionisation potential of the diene and the electron affinity of the dienophile is on the whole observed, there is no satisfactory correspondence between the quantities compared for the entire set of reactions under consideration. Detailed analysis demonstrates the existence of certain trends which can be explained if it is assumed that the reactivities of the addends are determined by the set of factors stabilising (donor–acceptor interactions) and destabilising (delocalisation) the transition state[60]. As already mentioned, the initial diene and dienophile systems undergo changes during the reaction corresponding to the delocalisation of the electrons in the 1,4-positions in the diene and the 1,2-positions in the dienophile and these changes are manifested in the energy of the transition state. In this connection one may note that, according to *ab initio* calculations for the reaction of butadiene with ethylene, its transition state is characterised by a considerable rearrangement of the initial systems and at the same time a low degree of formation of new bonds[3]. "From the standpoint of delocalisation", the reactivity of addends should be smaller the greater the delocalisation energy, i.e. the greater the energy expenditure required on the decomposition of the initial π-electron systems of the diene and dienophile on formation of the transition state and hence the adduct. Examination of the transition state stabilisation effects based on allowance for the donor–acceptor properties of the initial compounds ignores these differences between the addends. They can be taken into account by considering the enthalpies of the reactions of the diene–dienophile pairs which can serve as a measure of the delocalisation energies of the addends (Section VI).

The data in Figs. 14 and 15 are presented on the same scale and are comparable. The rate constants for reactions of different series refer to several different temperatures (20°, 25°, and 30 °C), because the activation parameters for the recalculation of the constants in conformity with the Arrhenius or Eyring equation were not available in all cases. There are also differences between the solvents. The calculation performed taking into account the activation parameters for similar reactions and with a known (low) sensitivity of the reaction rate constants to the nature of the solvent have shown that the above differences can lead to differences of the order of 0.3–0.5 in $\lg k$ for different reaction series. This does not exceed the limits of the errors within which the given problem is considered (among all the quantities used for the given study, the electron affinity is determined least accurately). The ionisation potentials and the electron affinities employed are listed in Tables 5 and 6 and were taken from the literature[16,17,25,27,64,65,73,74].

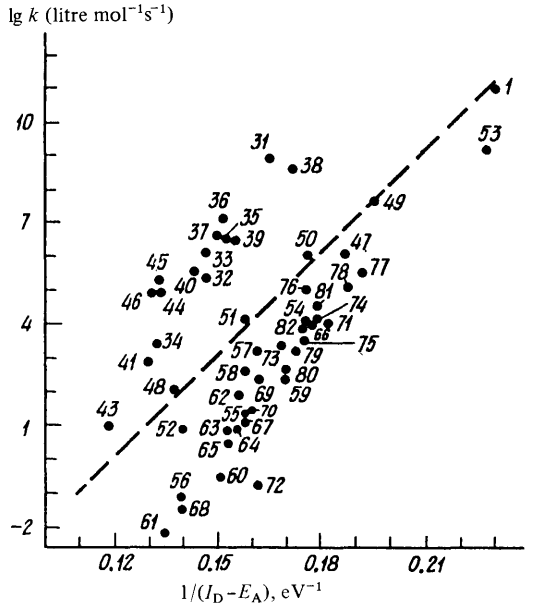


Figure 15. Dependence of $\lg k$ on $1/(I_D - E_A)$ for different diene–dienophile systems. Reactions of 1,3-diphenylisobenzofuran with dienophiles: 31) 1,1-dicyanoethylene; 32) fumarodinitrile; 33) maleodinitrile; 34) acrylonitrile; 35) maleic anhydride; 36) *N*-(*p*-nitrophenyl)maleimide; 37) *N*-phenylmaleimide (dioxane, 30 °C [16]). Reactions of cyclopentadiene with dienophiles: 38) tetracyanoethylene; 39) tricyanoethylene; 40) 1,1-dicyanoethylene; 41) fumarodinitrile; 42) maleodinitrile; 43) acrylonitrile (dioxane, 30 °C [75]); 44) maleic anhydride (dioxane, 30 °C [76]); 45) *N*-(*p*-nitrophenyl)maleimide; 46) *N*-phenylmaleimide (dioxane, 30 °C [19]). Reactions of cyclohexadiene with dienophiles; 47) tetracyanoethylene (methylene chloride, 20 °C); 48) maleic anhydride (dioxane, 30 °C [74]). Reactions of 9,10-dimethylanthracene with dienophiles: 1) tetracyanoethylene; 49) tricyanoethylene; 50) 1,1-dicyanoethylene; 51) fumarodinitrile and maleodinitrile; 52) acrylonitrile (dioxane, 20 °C [75]). Reactions of 9-methylanthracene with dienophiles: 53) tricyanoethylene; 54) 1,1-dicyanoethylene; 55) fumarodinitrile and maleodinitrile; 56) acrylonitrile (dichloroethane, 25 °C [77]); 57) *N*-(*p*-nitrophenyl)maleimide; 58) *N*-phenylmaleimide (dioxane, 25 °C [9]). Reactions of anthracene with dienophiles: 59) 1,1-dicyanoethylene; 60) fumarodinitrile and maleodinitrile; 61) acrylonitrile (dichloroethane, 25 °C [77]); 62) *N*-(*p*-nitrophenyl)maleimide; 63) *N*-phenylmaleimide (dioxane, 25 °C [9]). Reactions of 9-chloroanthracene with dienophiles: 64) *N*-(*p*-nitrophenyl)-maleimide; 65) *N*-phenylmaleimide (dioxane, 25 °C [9]). Reactions of 9-methoxyanthracene with dienophiles: 66) 1,1-dicyanoethylene; 67) 1,2-dicyanoethylene; 68) acrylonitrile (dichloroethane, 25 °C [9]); 69) *N*-(*p*-nitrophenyl)maleimide; 70) *N*-phenylmaleimide (dioxane, 25 °C [9]). Reactions of 9,10-dimethoxyanthracene with dienophiles: 71) 1,1-dicyanoethylene; 72) 1,2-dicyanoethylene (dichloroethane, 25 °C [77]). Reactions of tetracene with dienophiles: 73) maleic anhydride; 74) *N*-(*p*-nitrophenyl)maleimide; 75) *N*-phenylmaleimide. Reactions of pentacene with dienophiles: 76) maleic anhydride; 77) *N*-(*p*-nitrophenyl)maleimide; 78) *N*-phenylmaleimide. Reactions of 5,11-dichlorotetracene with dienophiles: 79) *N*-(*p*-nitrophenyl)maleimide; 80) *N*-phenylmaleimide. Reactions of 6,13-dichloropentacene with dienophiles: 81) *N*-(*p*-nitrophenyl)maleimide; 82) *N*-phenylmaleimide (toluene, 25 °C [25]).

We may draw attention to several phenomena which may be noted in the analysis of the data in Fig.14. The reactivity of butadienes in reactions with all three dienophiles investigated (tetracyanoethylene, maleic anhydride, and 4-phenyl-1,2,4-triazoline-3,5-dione) varies in such a way that the phenylated butadienes are less reactive than might have been expected on the basis of their electron-donating properties and the reactions with these butadienes are less exothermic (Table 5), which indicates higher delocalisation energies (Δh_{IBF} for 2,3-dimethylbuta-1,3-diene, *trans*-1-phenylbuta-1,3-diene, and *trans,trans*-1,4-diphenylbuta-1,3-diene are respectively −25.5, −17.5, and −6.7 kcal mol^{-1}). On the other hand, the differences between the reactivities of the three dienophiles examined are such that they correspond not only to the differences between their electron-accepting properties but also to the differences between the enthalpies of reaction (the Δh_{TCE} are 0, −3.9, and −8.5 kcal mol^{-1} respectively).

It is also striking that the reactivities of anthracenes in reactions with tetracyanoethylene and maleic anhydride (Fig.14) or arylmaleimides (Fig.15) differ very greatly, although the differences between their electron-donating properties are small. Furthermore, 9-methoxy- and 9,10-dimethoxy-anthracenes have particularly low reactivities. Overall, all anthracenes are less reactive than butadienes to a greater extent than might have been expected on the basis of their electron-donating properties. These phenomena are also understandable if account is taken of the observed differences between the enthalpies of the reactions (between the delocalisation energies) of these dienes.

Presumably the sensitivity to changes in the donor–acceptor interactions of the reactants is revealed most correctly in reaction series where the cyanoethylenes are varied. These compounds have very different electron-accepting properties, while the difference between their delocalisation energies is small (Table 6). The correlation straight line in Fig.15 corresponds to the 9,10-dimethylanthracene–cyanoethylenes reaction series. For comparison, it has been transferred to Fig.14 in the form of a dashed line.

Taking into account all the foregoing considerations, an attempt was made to examine the dependence of the reactivity of the same set of diene–dienophile systems on the set of donor–acceptor properties of the addends and their capacity for delocalisation in accordance with the equation

$$\lg k \propto /(I_D - E_A) - p\,\Delta H. \qquad (4)$$

Here both the parameter $1/(I_D - E_A)$ and ΔH reflect simultaneously the properties of both the diene and the dienophile.

According to Eqn.(4), the reactivity of the diene–dienophile system is greater the smaller the difference between the energies of the interacting orbitals ($I_D - E_A$) and the more exothermic the reaction (the higher the absolute value of ΔH).

Fig.16 illustrates the correlation between $\lg k$ and $1/(I_D - E_A) - 0.02\Delta H$§. The results obtained show that there is a large group of reactions (65 points refer to this group in Fig.16) which obey fairly satisfactorily the overall dependence of the reactivity of the diene–dienophile system on the parameters considered and for which the range of variation of the reaction rate constants amounts to 14 orders of magnitude. It includes the reactions of different dienophiles with butadienes and polynuclear compounds as the dienes.

§ In order to employ the experimental quantities directly in the given treatment, the calculation was performed for I_D and E_A expressed in eV and for ΔH expressed in kcal mol^{-1}. The adjustment of the measurements to the same system of units would require a simple alteration of the coefficients.

Compared with this group, an enhanced reactivity (for the same type of variation of the reactivity within the series) is shown in reactions involving cyclopentadiene and 1,3-diphenylisobenzofuran as dienes. This phenomenon can be explained if one takes into account the fact that the C(1)–C(4) distances in the dienes are different and that this influences their reactivity[78,79]; however, these distances are not apparently adequately reflected either in the electron-donating properties of the dienes or in the enthalpies of reaction.

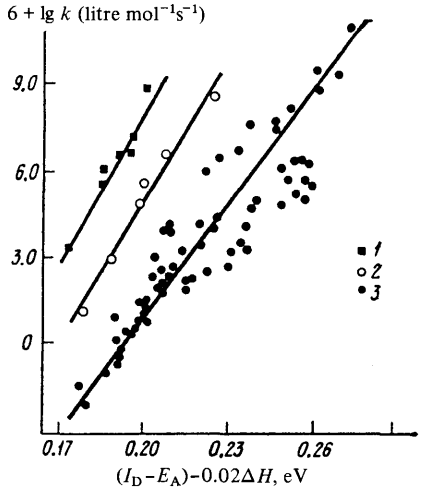


Figure 16. Dependence of the reactivity of addends in the diene synthesis reaction on the reciprocal of the difference between the ionisation potential of the diene and the electron affinity of the dienophile and on the enthalpies of reaction. Dienes employed: 1) cyclopentadiene; 2) 1,3-diphenylisobenzofuran; 3) butadienes and polynuclear compounds.

The view has been expressed that the role of the effects of the donor–acceptor interaction and delocalisation can change as a function of the position of the transition state on the reaction coordinate[80,81,73]:

$$\lg k \propto \alpha[1/(I_D - E_A)] + (1-\alpha)\Delta H,$$

where α varies from 1 to 0 along the reaction coordinate on passing from the starting materials to the products. Accordingly, the data for the reactions presented in Fig.16 were treated in terms of the equation

$$\lg k = 1/(I_D - E_A) - q(I_D - E_A)\cdot\Delta H,$$

according to which the sensitivity to the localisation effects depends on the intensity of the donor–acceptor interaction. The greater this intensity, the smaller the multiplier equal to the difference $I_D - E_A$. In this case the agreement between the calculated and experimental quantities is impaired. At present it would be premature to reach definite conclusions on the basis of these results. It is more correct to regard them as preliminary and to assume that they require further refinement. However, the main conclusion is not subject to any doubt, since both the energies of the donor–acceptor interaction and the delocalisation energies influence the reactivity of the diene–dienophile systems, constituting the principal electronic factors determining the reactivity of the addends.

Depending on the relative donor–acceptor interaction and delocalisation energies, there is a possibility of different combinations of the reactions[59,82], which are illustrated schematically in Fig.17 by energy profiles which refer to the two processes compared and differ only in the dienes or dienophiles; they can model the reaction series. The decrease of the energy in the prereaction state on the profiles corresponds to the donor–acceptor interactions and the relative positions of the final states correspond to the differences between the delocalisation energies of the addends. The combinations of the reactions can be divided into several types.

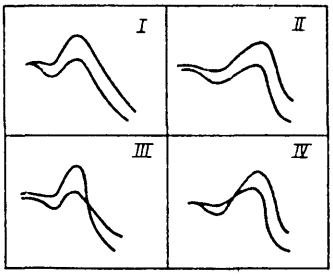


Figure 17. Energy profiles of reactions with different ratios of the donor–acceptor interaction and delocalisation energies (see text).

I. The donor–acceptor interaction and delocalisation energies vary in parallel from the standpoint of the influence on the rate of reaction; the relative reactivity of the addends is controlled by the donor–acceptor interactions. In this case the energy profiles of the reactions do not intersect and the stability of the adducts corresponds to the reactivity of the addends.

II. The donor–acceptor interaction and delocalisation energies vary in parallel, but the relative reactivity of the addends is controlled by delocalisation effects. In this case the energy profiles of the reaction also do not intersect and the stability of the adducts corresponds to the reactivity of the addends.

III. There is an antiparallel variation of the donor–acceptor interaction and delocalisation energies and the relative reactivity of the addends is controlled by the donor–acceptor interactions. In this case the energy profiles of the reactions intersect in the region of energies beyond the activation barrier; the stability of the adducts is inconsistent with the reactivity of the addends.

IV. There is an antiparallel variation of the donor–acceptor interaction and delocalisation energies and the relative reactivity is controlled by delocalisation effects; the energy profiles of the reactions intersect in the range of energies before the activation barrier; the stability of the adducts corresponds to the reactivity of the addends.

Without classifying the entire set of reactions in terms of the types indicated, it is possible to consider certain examples.

Reactions with strongly electron-donating dienes and electron-accepting dienophiles, in particular, the reactions of *meso*-substituted anthracenes with tetracyanoethylene in which the relative reactivity of anthracene corresponds to their electron-donating properties[63] and the "more reactive the reagent the greater its selectivity" rule holds[77] (see Section VIII) can be assigned to type I.

Reactions of type II are difficult to identify definitely. The study of the relation between reactivity and selectivity suggests that this type holds in reactions of arylmaleimides with anthracenes[9].

A striking example of reactions of type III is provided by the interaction of cyanoethylenes with any of the electron-donating dienes (cyclopentadiene, anthracenes, and isobenzofuran). The antiparallel variation of the electron-accepting properties and localisation energies of cyanoethylenes has been demonstrated by both quantum-chemical calculations[60,66] and by experimental data (Table 6). The reactivity of cyanoethylenes corresponds to their electron-accepting properties and increases from acrylonitrile to tetracyanoethylene, while the localisation energies (enthalpies of reaction) vary in the opposite sequence, which is consistent with the variation of the stabilities of the adducts demonstrated in relation to the reactions with 9,10-dimethoxyanthracene[69]. The reactions of butadiene or 1,4-diphenylbutadiene with tetracyanoethylene belong to type III. In this pair of reactions, 1,4-diphenylbutadiene, the more electron-donating diene, is more reactive (Table 3).

The replacement of tetracyanoethylene by maleic anhydride in reactions with the same dienes (butadiene and 1,4-diphenylbutadiene) leads to reactions of type IV. Butadiene, which is less electron-donating but has a smaller localisation energy, is more reactive. When the dienophile is altered, the donor–acceptor interaction energy changes (decreases) and the factor controlling the relative reactivity of the reactant (diene) is changed. Another example of the combination of type IV reactions may be provided by the reactions of butadienes with 4-phenyl-1,2,4-triazoline-3,5-dione compared with the reactions of the same butadienes with tetracyanoethylene. Tetracyanoethylene is more electron-accepting, but it is less reactive for "localisation" reasons. Incidentally, it is of interest also to compare the reactivities of the above dienes (butadiene and 1,4-diphenylbutadiene) in the reactions with 4-phenyl-1,2,4-triazoline-3,5-dione. In this case the reactivities of these dienes are comparable, in conformity with the "intermediate" electron-accepting properties of the dienophile.

Thus the donor–acceptor properties and localisation energies quoted as the two principal electronic factors in the study of the reactivities of addends explain many phenomena which previously appeared obscure.

VIII. THE SELECTIVITY OF ADDENDS IN THE DIENE SYNTHESIS REACTION

The selectivity S in reactivities is understood as the difference between the reactivities ($\lg k$) in the interaction of the given reactant with two others having different reactivities. On the basis of a study by the present author and his co-workers[77], we shall examine the pairs of reactions of two electron donors D_1 and D_2 with two electron acceptors A_1 and A_2. Then

$$S_{D_1} = \lg k_{D_1}^{A_1} - \lg k_{D_1}^{A_2};\ S_{D_2} = \lg k_{D_2}^{A_1} - \lg k_{D_2}^{A_2}$$

and the relative selectivity of the electron donors is described by the expression

$$S_{D_2}^{D_1} = S_{D_1}/S_{D_2} = (\lg k_{D_1}^{A_1} - \lg k_{D_1}^{A_2})/(\lg k_{D_2}^{A_1} - \lg k_{D_2}^{A_2}).$$

Similarly, for electron acceptors we have

$$S_{A_2}^{A_1} = S_{A_1}/S_{A_2} = (\lg k_{D_1}^{A_1} - \lg k_{D_2}^{A_1})/(\lg k_{D_1}^{A_2} - \lg k_{D_2}^{A_2}).$$

We shall assume that the electron-donating properties of D_1 are more prounced than those of D_2 and the electron-accepting properties of A_1 are more pronounced than those of A_2, which implies that $\varepsilon_{D_1}^{HOMO} > \varepsilon_{D_2}^{HOMO}$ (or $I_{D_1} < I_{D_2}$) and $\varepsilon_{A_2}^{LUMO} < \varepsilon_{A_2}^{LUMO}$ (or $E_{A_1} > E_{A_2}$). We shall consider the differences between the reactivities which are due to the differences between the energies of the donor–acceptor interactions [in conformity with the relation $\lg k_D^A \propto 1/(I_D - E_A)$]. Then

$$S_{D_2}^{D_1} = \frac{(I_{D_2} - E_{A_1})(I_{D_2} - E_{A_2})}{(I_{D_1} - E_{A_1})(I_{D_1} - E_{A_2})} ;$$

$$S_{A_2}^{A_1} = \frac{(I_{D_1} - E_{A_2})(I_{D_2} - E_{A_2})}{(I_{D_1} - E_{A_1})(I_{D_2} - E_{A_1})} .$$

For the conditions adopted above, we have the following relations:

$$(I_{D_2} - E_{A_1}) > (I_{D_1} - E_{A_1}); \quad (I_{D_2} - E_{A_2}) > (I_{D_1} - E_{A_2});$$
$$(I_{D_1} - E_{A_2}) > (I_{D_1} - E_{A_1}); \quad (I_{D_2} - E_{A_2}) > (I_{D_2} - E_{A_1}) .$$

Hence

$$S_{D_2}^{D_1} > 1, \quad S_{A_2}^{A_1} > 1 ,$$

i.e. the donor with more marked electron-donating properties and hence the acceptor with more pronounced electron-accepting properties should be more selective. In those cases where the relative reactivity of the addends is controlled by their donor–acceptor properties, this implies that the more reactive reactant should be more selective. This type of relation between reactivity and selectivity has been demonstrated for a whole series of examples of reactions of both the "diene (donor)–dienophile (acceptor)" type[20,24,77] and the "diene (acceptor)–dienophile (donor)" type[40]. Fig.18 presents data referring to the reactions of *N*-arylmaleimides with acenes.

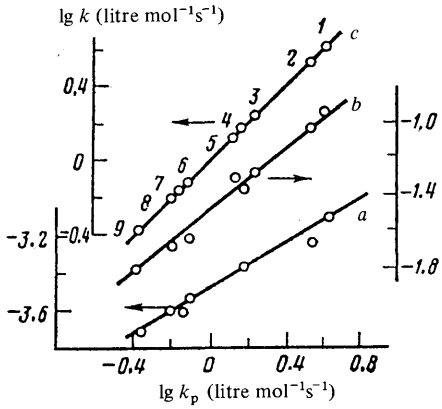


Figure 18. Dependence of the reactivities of *N*-(XC_6H_4)-substituted maleimides [X: 1) *m*-NO_2; 2) *p*-NO_2; 3) *p*-CH_3OCO; 5) *m*-Cl; 6) H; 7) *p*-CH_3; 8) *p*-CH_3O; 9) *p*-$(CH_3)_2N$] in reactions with anthracene (*a*), tetracene (*b*), and pentacene (*c*) on their reactivities in the reactions with pentacene ($\lg k_p$) (toluene, 60 °C).

The rule which states that "the more reactive the reactant the greater its selectivity" holds also in reactions of the "neutral"type in those cases where one of the donor–acceptor interactions between the addends exerts a preferential influence[34,39].

In those reactions where the relative reactivity is controlled by the delocalisation energies of the addends, the relation between reactivity and selectivity may be different, but in this instance too the selectivity of the reactants depends on their donor–acceptor properties. In this connection it is of interest to compare the variation of the reactivities and selectivities of three dienophiles: maleic anhydride, tetracyanoethylene, and 4-phenyl-1,2,4-triazoline-3,5-dione in reactions with buta-1,3-diene, 2-methylbuta-1,3-diene, and 2,3-dimethylbuta-1,3-diene (Fig.19, see also the data in Table 3). Tetracyanoethylene is more reactive and more selective than maleic anhydride. The relative reactivities of these dienophiles are controlled by the effects of the donor–acceptor interactions (tetracyanoethylene is significantly more electron-accepting than maleic anhydride but has a higher delocalisation energy). 4-Phenyl-1,2,4-triazoline-3,5-dione is more reactive than tetracyanoethylene (the relative reactivity is controlled in this instance by the delocalisation energies), but, in conformity with its electron-accepting properties, it occupies an intermediate position as regards selectivity between tetracyanoethylene and maleic anhydride. Another clear example is provided by the reactivities of cyanoethylenes in their interaction with substituted phencyclones (Section IX).

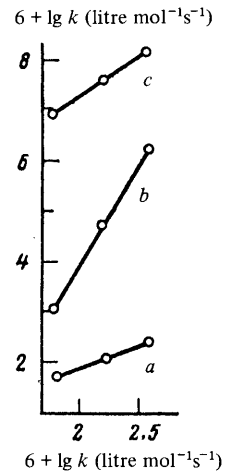


Figure 19. Dependence of the reactivities of maleic anhydride (*a*), tetracyanoethylene (*b*), and 4-phenyl-1,2,4-triazoline-3,5-dione (*c*) in the diene synthesis reactions with a series of dienes [1) butadienes; 2) isoprene; 3) 2,3-dimethylbutadiene] on the reactivities of these dienes in reactions with maleic anhydride ($\lg k_{MA}$).

IX. CYANOETHYLENES IN THE DIENE SYNTHESIS REACTION. QUALITATIVE DIFFERENCES BETWEEN THE EFFECTS OF THE INTERACTION OF ANTISYMMETRIC AND SYMMETRICAL FRONTIER ORBITALS

As mentioned above (Sections III and VII), the reactivities of cyanoethylenes in reactions with typical electron-donating dienes vary in accordance with their electron-accepting properties (electron affinities). It has been found that this

behaviour of cyanoethylenes is not always observed. Interesting data have been obtained in the study of their reactions with substituted phencyclones[83,84]:

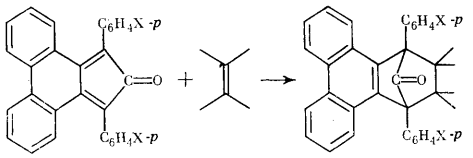


Fig. 20, which presents the corresponding correlation plots, shows that the variation of the reactivities of substituted phencyclones in reactions with each cyanoethylene is described satisfactorily by the Hammett σ constants (r varies from 0.993 to 0.999) with $\rho < 0$. In conformity with the conclusions reached in Section VIII, the absolute value of ρ (the selectivity) is then greater the more pronounced the electron-accepting properties of the cyanoethylene (Fig. 21), which indicates that the reaction is of the "diene (donor)–dienophile (acceptor)" type.

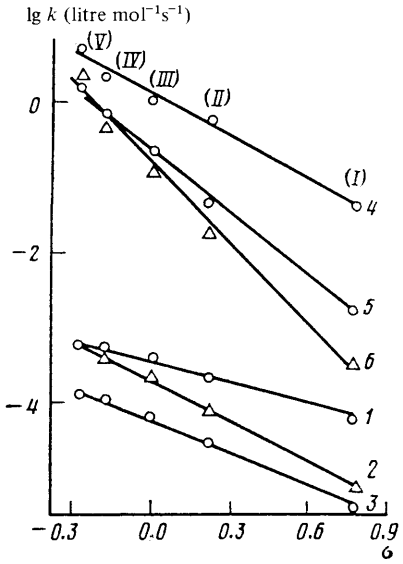


Figure 20. Dependence of lg k for the substituted phencyclones (I)–(V) in the reactions with cyanoethylenes (lines *1*–*6*) on the Hammett σ constants (chlorobenzene, 30 °C). Substituents X in phencyclones: I) p-NO_2; II) p-Cl; III) H; IV) p-CH_3; V) p-CH_3O. Cyanoethylenes: 1) acrylonitrile; 2) maleodinitrile; 3) fumarodinitrile; 4) 1,1-dicyanoethylene; 5) tricyanoethylene; 6) tetracyanoethylene.

On the other hand, the relative reactivities of cyanoethylenes in the reactions with each phencyclone vary in an unusual manner. The reactivities do not correspond explicitly to one particular reaction type and depend on the electron-accepting character of the substituent in the cyclone. The possible causes capable of giving rise to this phenomenon have been analysed[83,84]. The behaviour of cyanoethylenes becomes understandable if it is assumed that their reactivites are determined not only by the electron-accepting properties but also by the delocalisation energies.

Table 8 presents equations describing the variation of the reactivities of cyanoethylenes taking into account their electron affinities and localisation energies in reactions with each phencyclone investigated. It is striking that, on passing from the phencyclone containing the electron-donating CH_3O substituent to one with the electron-accepting NO_2 substituent, the sensitivity of the diene to the localisation effects of the dienophiles increases. Taking into account the fact that the phencyclone containing the carbonyl group exhibits electron-accepting properties, the general conclusion that an enhancement of the electron-accepting properties of the dienes entails an increase of their sensitivity to the effects of the localisation of the dienophiles becomes apparent.

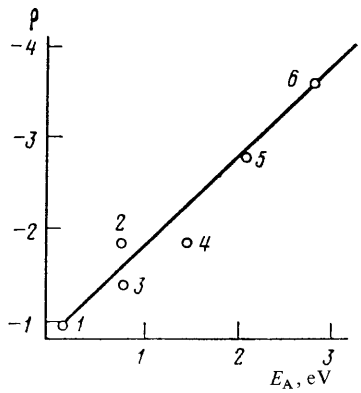
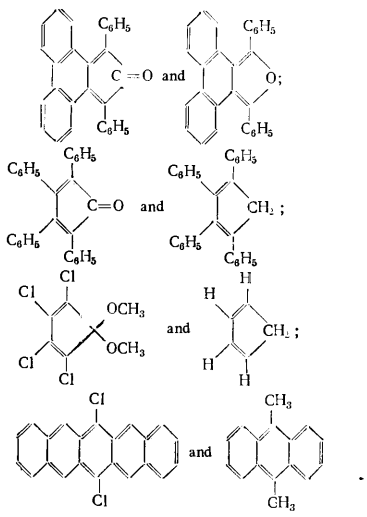


Figure 21. Dependence of the reaction constants for the reactions of substituted phencyclones with cyanoethylenes on the electron affinity of the dienophiles (chlorobenzene, 30 °C). The numbering of the dienophiles is the same as in Fig. 20.

The validity of this conclusion is demonstrated by the results of the study of the reactivities of cyanoethylenes with respect to the following pairs of dienes, having similar structures but differing in their electronic properties[83–88]:



The variation of the reactivities of cyanoethylenes in reactions with electron-donating dienes is determined by the electron-accepting properties of the dienophiles. In the reactions with electron-accepting dienes account must be taken of their localisation properties. A similar behaviour has been observed also in the reactions of substituted phencyclones with arylmaleimides and maleic anhydride[89].

Table 8. Correlation between the reactivities of cyanoethylenes as dienophiles in reactions with substituted phencyclones (k, litre mol^{-1} s^{-1}), and the electron affinities (E_A, β) and localisation energies (L, β) of the dienophiles (β is the resonance integral).

Substituent X in phencyclone	Equation	r
p-CH_3O	$\lg k = 30.16\,E_A - 6.64\,L + 33.39$	0.992
p-CH_3	$\lg k = 28.31\,E_A - 6.51\,L + 32.30$	0.986
H	$\lg k = 27.91\,E_A - 6.70\,L + 32.45$	0.986
p-Cl	$\lg k = 28.30\,E_A - 7.08\,L + 33.93$	0.986
p-NO_2	$\lg k = 27.03\,E_A - 7.54\,L + 33.78$	0.984

For further study, it is important to note that, according to the data in Section V, in reactions of the "neutral type" the dienes are as a rule electron-accepting in relation to the dienophiles (cyclones, dichloroacenes, and halogeno-*o*-quinones in reactions with styrenes). This makes it necessary to suppose that the interactions of the HOMO of the diene with the LUMO of the dienophile and of the HOMO of the dienophile with the LUMO of the diene are non-equivalent. The interaction of the HOMO of the diene with the LUMO of the dienophile is seen to be preferred.

On the basis of a theoretical analysis, it has been suggested[90,91] that there are fundamental differences between the interactions of the HOMO of the diene and the LUMO of the dienophile (antisymmetric orbitals), on the one hand, and of the HOMO of the dienophile and the LUMO of the diene (symmetrical orbitals), on the other. In the former case the electron density is concentrated between the reaction centres, ensuring conditions for the formation of the chemical bond. A change in the coordinates of the atomic nuclei promotes the reaction (Fig. 22). In the latter case, as a consequence of the resolution of the cross-overlapping, the electron density is concentrated in the central part of the intermolecular space and the changes in the coordinates of the atomic nuclei are not favourable for the reaction. Therefore, even in those cases where the interaction of the symmetrical orbitals predominates, the authors[90,91] believe that the interaction of the antisymmetric orbitals is responsible for the occurrence of the reaction (i.e. for the formation of new bonds). The interaction of symmetrical orbitals promotes the stabilisation of the prereaction charge-transfer complex (and to some extent of the transition state), but requires the localisation of the electrons on the reaction centres for the reaction to occur.

This approach explains also the characteristic features of reactions of the "neutral type" and of the more pronounced dependence of the reactivity of the addends on the delocalisation effects when the electron-accepting character of the diene becomes more marked, as well as the observed antiparallel variation of the stabilities of the charge-transfer complexes between the addends and their reactivities in reactions of the "diene (acceptor)–dienophile (donor)" type[92], in contrast to the parallel variation of these properties in reactions of the "diene (donor)–dienophile (acceptor)" type (Section V).

It is noteworthy that, when the interaction of the symmetrical orbitals predominates in the Diels–Alder reaction, the mechanism of the latter can change. Whereas the interaction of the antisymmetric orbitals promotes a synchronous reaction, the dominant interaction of symmetrical orbitals can lead to a two-stage reaction with formation of an intermediate. The available data, indicating the infringement of the "*cis*-principle" in reactions involving electron-accepting dienes such as hexahclorocyclopentadiene[93], acridizinium ions[94,95], and phenyldiazenium salts[96] provide an example of such behaviour. Despite the symmetry of the reactants, instances of the breakdown of the "*cis*-principle" have not so far been observed in reactions of the "diene (donor)–dienophile (acceptor)" type[1,97].

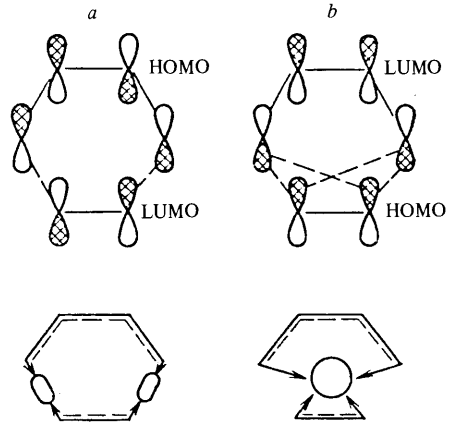


Figure 22. Schematic representation of the interaction of antisymmetric (*a*) and symmetrical (*b*) frontier orbitals of the addends in Diels–Alder reactions.

The change in the electronic character of the reactant and the associated change in sensitivity to the localisation effects can alter also the periselectivity of the reaction. It is well known that electron-donating dienes react with tetracyanoethylene at a carbon–carbon bond[98–100]. However, this dienophile reacts with electron-accepting dienes under mild conditions to form products of addition to the cyano-group[101,102]. Acrylonitrile behaves analogously[103]. Such behaviour corresponds to the lower stability (lower delocalisation energy) of the C≡N bond compared with the C=C bond.

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The above discussion shows that many characteristic features of the reactivities of the addends in diene synthesis can be explained if the donor–acceptor properties and stabilities of the reactants, described by the delocalisation energies or enthalpies of reaction, are adopted as the principal electronic factors determining the reactivities of dienes and dienophiles. The enthalpies of reaction make it possible to take into account also the differences between the energies of the *s-trans–s-cis* conformational transitions, which influence the reactivities of open-chain dienes. On the other hand, the

geometrical factor, such as the 1,4-distances in dienes, needs to be taken into account as well. It is noteworthy that the above conclusion has been reached on the basis of the study of reactions of the "diene (donor)–dienophile (acceptor)" type. In order to answer the question to what extent this conclusion is valid for reactions of other types, special studies are necessary. Data indicating the possible qualitative differences between the effects of the interaction of the antisymmetric and symmetrical orbitals make it particularly necessary.

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Conformations of Six-membered Carbon Rings with Planar Groups

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A systematic account is given of experimental and theoretical data on the steric structures of six-membered rings containing groups with a coplanar disposition of three consecutive bonds within the ring—a fragment with a double bond, a condensed rigid ring, or a bridged bicyclic system. We shall consider rings containing one such fragment, namely cyclohexane, bicyclo-[4.1.0] heptane, and its analogues, as well as rings with two fragments of this kind in the 1,4- or 1,3-positions. Data are presented on the structure of the rings, their inversion, and the orientation of the substituents in various positions. The principal characteristics of the conformational structures of such compounds are described and the possibility of the assumption of the boat form and the relative preferences for the axial and pseudoaxial orientations of the substituents and the condensed planarising fragments are discussed.
The bibliography includes 272 references.

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I. INTRODUCTION

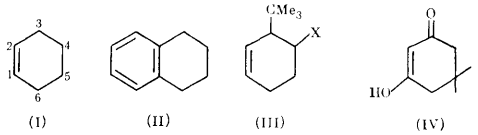
Cyclohexane and its derivatives are classical objects of conformational analysis. Much less attention has been devoted to six-membered carbon rings with planar groups of atoms formed by a double bond or by condensation with a rigid system ensuring an eclipsed conformation of the common bond. The ring may also contain two planar groups in the 1,3- or 1,4-positions. Variation of the nature and positions of such groups and of the configurations of the condensed rings and substituents creates a wide variety of possible types of compounds. Studies on such compounds have been far from uniform; the available reviews concern individual conformational relations for the cyclohexane[1,2] and cyclohexa-1,4-diene[3,4] series.

The stereochemistry of both unsaturated six-membered rings and cyclohexanes or cyclohexenes condensed with three-membered rings or other rigid systems has developed vigorously during the last decade. A theoretical basis for the known facts is being developed and a number of common features have been discovered. This permits a survey and analysis of the results obtained.

II. PRINCIPAL CHARACTERISTICS OF THE CONFORMATIONAL STRUCTURE OF CYCLOHEXENES

1. Ring Conformation

It is known that cyclohexene (I) and its derivatives exist in the half-chair conformation (Fig.1).[5,6] The endocyclic torsional angles ϕ(for the half-chair conformation the angle of twist ψ) serve as a measure of non-planarity. The structure of cyclohexene has been determined by gas electron diffraction[7-11] and microwave spectroscopy[12,13]:



(I) (II) (III) (IV)

The angles ϕ vary within narrow limits: $\phi(23) = 15.2-15.7°$, $\phi(34) = 44.8-46.0°$, $\phi(45) = 60.2-62.6°$, and $\psi = 25.4°$ (Chiang and Bauer[10]) or 30.1° (Scharpen et al.[13]). The value $\phi(45) = 63°$ was also established by ^{1}H NMR.[14] Theoretical conformational analysis using various computational methods leads to a good agreement with experiment[8,9,15-23]. Ring structure is retained when the substituents are located only at the olefinic atoms in cyclohexene, in tetralin (II), and in its heteroaromatic analogues; a number of data have been published for tetralin derivatives[24,25] and for their solutions[26].

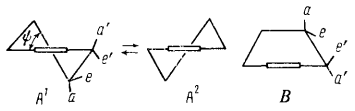


Figure 1. The conformations of cyclohexene and its derivatives; A^1, A^2—half-chair; B—boat.

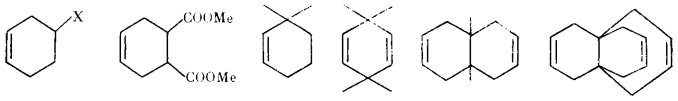
Asymmetric substitution can distort the half-chair, i.e. can lead to different deviations of the C(4), and C(5) atoms from the plane of the double bond, which has been demonstrated by calculation[18,27] and structural studies[24,25]. Marked distortions are observed under the conditions of steric hindrance due to bulky substituents. For example, the angle ϕ(23) in the *trans*-isomers of 4-substituted 3-t-butylcyclohexenes (III) and the angle ϕ(56) in the *cis*-isomers diminish to 7°.[28,29] Further distortion of the half-chair leads to the boat conformation, which has been observed for certain polycyclic compounds[32].

An additional conformational effect, namely conjugation of the C=O bond with the π-electron system, is observed in cyclohexanones and tetralinones. This effect stabilises the 1,2-diplanar form (the envelope conformation); thus the C(5) atom in dimedone (IV) is displaced from the plane of the ring by 0.6 Å.[30,31] The structure of 1-tetralinone is also close to the envelope conformation[32].

2. Ring Inversion

The barrier $\Delta G^{\neq}$ to the transition between two half-chairs A^1 and A^2 in cyclohexene (Fig.1) amounts to 5 kcal mol^{-1} [33] or 7.6 kcal mol^{-1}. [34] The calculated data correspond to the maximum energy of the boat conformation. A point on the sloping section of the energy curve corresponds to the envelope conformation; the energy gain compared with the half-chair conformation is 1.5–2.5 kcal mol^{-1}. [17,22,35,36]

Data concerning the influence of substituents are contradictory. Energy barriers not exceeding 5.1 kcal mol^{-1} have been measured by the ultrasonic method for 4-substituted cyclohexenes (V): [37]



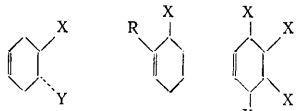
(V) (VI) (VII) (VIII) (IX) (X)

However, ^{1}H NMR studies of compounds (V) and (VI) have shown that the introduction of each substituent increases the barrier by 1 kcal mole^{-1}, which indicates inversions via the boat form[38]. This is confirmed by the increase of $\Delta G^{\neq}$ by 2.2 kcal mol^{-1} on passing from (VII) to (VIII)—the 3,6-flagstaff ("prow") interaction creates a considerable steric hindrance in the intermediate boat form[39]. Finally, the barrier for compound (IX) is approximately twice as high and that for compound (X) three times as high as the usual value, since two or three rings pass simultaneously through the boat form in the inversion process[40].

3. Conformations of the Substituents

The introduction of a double bond into a six-membered ring alters the orientation of the exocyclic bonds, particularly in the allylic positions, where they have a pseudoequatorial (*e'*) or pseudoaxial (*a'*) orientation (Fig.1). The dihedral angles between the planes in which these bonds are located (τ) differ appreciably from the angles in cyclohexane derivatives: $\tau(e'a) = 51°$, $\tau(e'e) = 62°$, $\tau(a'a) = 151°$, $\tau(a'e) = 53°$, $\tau(ea) = 64°$, and $\tau(aa) = 168°$. The bonds between the olefinic atoms form dihedral angles of 46° and 65° with the *e'*- and *a'*-substituents respectively[41]. The introduction of a double bond is responsible for the disappearance of one *syn*-axial interaction and a marked weakening of the second (*aa'*). The conformational energies of 4-substituents are therefore much lower than in the cyclohexane series. For halogen atoms, they are close to zero[38,42–46], and for iodine the *a*-orientation is actually preferred (ΔG = −0.05 kcal mol^{-1}). [38] The same may be noted for the cyano- and nitro-groups[46–48]. The methyl group[49] and the carbonyl functional groups[47,50–52] exhibit a somewhat greater tendency towards an equatorial orientation (but not exceeding 1 kcal mol^{-1}). The stabilisation of the axial position compared with the saturated analogues increases by 0.7 kcal mol^{-1} on passing from atom to atom in the series of halides, in conformity with their polarisabilities[38].

The $ee \rightleftharpoons aa$ equilibrium is possible for *trans*-4,5-disubstituted cyclohexenes (XI). In the case of dichlorides and dicyanides the proportions of different forms are virtually the same[53–56], while for X = Y = Br the repulsion of the equatorial substituents leads to a greater stability of the diaxial conformation[57–59]. On the other hand, *trans*-4,5-dimethylcyclohexene has a preferred diequatorial conformation (ΔG = 1.1 kcal mol^{-1}) [60,61] like the analogous acids and esters[62]. In contrast to compound (XI), *trans*-2,3-dihalogenotetralins are characterised by a greater proportion of the *aa*-form (up to 80% for X = Cl and 95% for X = Br. [26,57,63]



(XI) (XII) (XIII)

An extensive investigation of cyclohexane with various *trans*-substitutents in the 4,5-positions has been undertaken [47,50,64–68]. It has been established that compounds with carboxy-groups are fully diequatorial, while others are almost so. An appreciable shift is observed when one of the substituents is CCl_3 (up to 66% of the *aa*-conformer for X = CCl_3 and Y = CH_2OH). [66,67]. This resembles the behaviour of iodocyclohexene. The large bulk of the substituent is not an obstacle to its axial orientation; even the t-butyl group can occupy the *a*-position to a large extent[69].

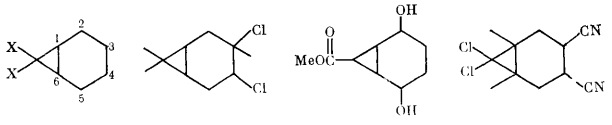
Pseudoequatorial substituents in the 3- and 6-positions are located close to the plane of the double bond, which is sterically unfavourable, particularly in the presence of substituents at the nearest olefinic atom, as in compound (XII). Such interaction is called 1,2-allylic ($A^{1,2}$). [1] The pseudoaxial position is therefore preferred for chlorine and bromine [43,70] and for certain oxygen-containing functional groups[71]. Qualitative analysis of the available data has shown that the proportion of the *e'*-conformer is greater only for 3-methylcyclohexene[72]. The *trans*-3,6-disubstituted derivatives can be fully diaxial[73]. 2,3-Disubstituted cyclohexenes are almost entirely pseudoaxial[74]. There is evidence that such orientation is caused not only by steric factors but also by hyperconjugation[72].

The different conformational conditions for the substituents in the 4(5)- and 3(6)-positions are revealed in the analysis of the structures of molecules of type (XIII), which exist in the form of six-configurational isomers. The *trans*-oriented bonds of the substituents at the atoms in the 4- and 5-positions assume the diequatorial position with the exception of the $a'eea' \rightleftharpoons e'aae'$ equilibrium, but even the latter is 80–90% displaced towards the first form[24,25,41,75–77]. Concordant results have been obtained by calculation for 3,4-dimethylcyclohexene: $ee' > ea' > ae' > aa'$. [21]

III. CONFORMATIONS OF CYCLOHEXANE FRAGMENTS IN BICYLIC SYSTEMS

1. Bycyclo[4.1.0]heptane

The condensation of a six-membered ring with a three-membered ring also gives rise to the coplanarity of four atoms and the loss of a plane of symmetry by the planar group leads to the presence of two different boat conformations (*syn*- and *anti*) and, in the presence of different substituents, also to two half-chair forms (Fig.2). Theoretical calculations predicted the maximum stability of the half-chair conformation of bycyclo[4.1.0]heptane (XIV, X = H), [78,79] but the energy of the boat form is not higher by more than 3.3 kcal mol^{-1}. An electron diffraction study yielded the same results[80] as for the 7,7-dichloro-derivative (XIV, X = Cl) [81,82] and *trans*-3,4-dichorocarane (XV): [83]



(XIV) (XV) (XVI) (XVII)

The half-chair conformation has been found by X-ray diffraction for many compounds, for example, for compound (XVI)[84] and a series of cyclosteroids[24,25]. As a rule, the half-chair is somewhat asymmetric and approaches the envelope form in polysubstituted compounds of type (XVII).[85] This has also been observed after the introduction of an sp^2-atom into the six-membered ring[86].

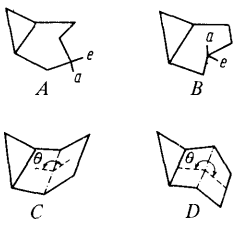


Figure 2. The possible conformations of bicyclo[4.1.0]-heptane; *A*, *B*—half-chair; *C*—*syn*-boat; *D*—*anti*-boat.

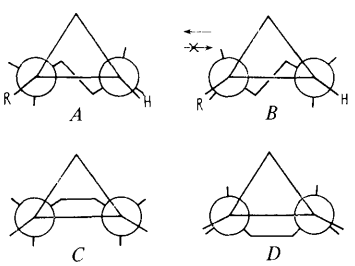
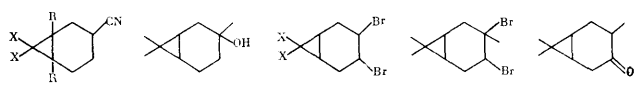


Figure 3. The orientation of the bonds in bicycloheptane systems; for legend, see Fig. 2.

Substituents in the 1-positions stabilise the half-chair form, in which they are less eclipsed (Fig. 3*A*). This has been demonstrated[87] for 1-t-butylbicycloheptane. The equatorial *cis*- and *trans*-substituents in the 3- and 4-positions do not interact with the ring, but the *cis*-axial substituent can be strongly destabilised, particularly for bulky *syn*-7-substituents. In the *trans*-isomers of compound (XVIII, R = H or Me, X = Cl or Br), the cyano-group is therefore 8% axial, while in the *cis*-isomers it occupies only the equatorial position[88,89]; similarly in both caranol (XIX) isomers the *cis*-substituent is equatorial[90,91]. Only the methoxycarbonyl group retains the equatorial position whatever the configuration[92,93].



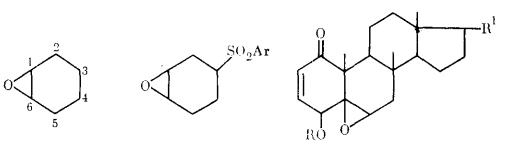
In *trans*-3, 4-disubstituted bicycloheptanes, the unsubstituted three-membered ring does not hinder the diaxial conformation; at any rate, in dibromocycloheptane the latter predominantes significantly[94]. In 1,6-disubstituted derivatives the steric hindrance experienced by the *trans*-axial substituent results in a diequatorial structure of the 3,4-diesters[89,92,95] and the corresponding dinitriles[89].

The introduction of substituents into the *syn*-7-position increases the conformational possibilities. The distortion of the ring in compound (XVII) in the direction of the envelope form in the crystalline phase has been noted. The tetrahalogeno-compounds (XX, X = Cl or Br) exist in solution mainly in the *anti*-boat conformation with the angle $\theta = 200$ to 215 °C.[96] The same form appears in the equilibrium involving dibromocarane (XXI) although the dichloro-derivative consists of a mixture of the *ee*- and *aa*-half-chair conformations: the smaller chlorine atom can be in the *cis*-axial position relative to the *gem*-dimethyl group[97,98]. The *anti*-boat conformation appears also in caranols and caramines with the *cis*-orientation of two substituents in the 3- and 4-positions[99,100]; the conformation of compounds of this type is greatly influenced by the possibility of the formation of hydrogen bonds[101–104].

The half-chair conformation is retained when sp^2-atoms are introduced into the ring[105,106] and in the isomeric caranones (XXII) the carbonyl group approaches the three-membered ring regardless of the orientation of the 3-methyl group[105].

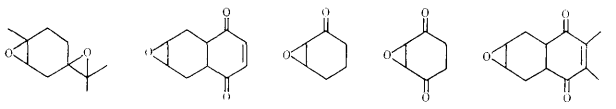
2. 7-Heteroanalogues of Bicycloheptane

Epoxycyclohexane (XXIII) has been investigated by gas electron diffraction[7,107,108] and microwave spectroscopy[109]. The six-membered ring has the half-chair conformation with the endocyclic dihedral angles $\phi(12) = \phi(65) = 16.3°$, $\phi(23) = \phi(54) = 48.8°$, $\phi(34) = 63.9°$,[108] and $\psi = 34.4°$.[109]



The results of calculations by the method of molecular mechanics are consistent with these findings[79]. The half-chair conformation has been established for many epoxycyclohexanes, for example, the isomers of compound (XXIV)[110] and polysubstituted and polycyclic compounds[24,25], including steriods. It is noteworthy, firstly, that the half-chair is usually asymmetric and, secondly, that its form depends to a large extent on the strength of the crystal field. Thus withafevin A (XXV) crystallises in two conformations differing in the direction and degree of bending of the *B* ring[111].

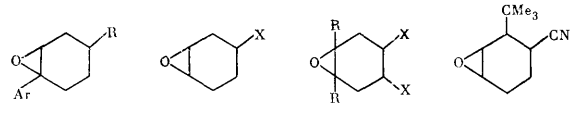
In certain epoxides the cyclohexane ring has the boat conformation. The electrical parameters of the molecule of terpinolene dioxide (XXVI) can be described only in terms of the presence of this form[112]. The boat conformation is to some extent stabilised by the other six-membered ring: for this reason, 10–20% of the *syn*-boat conformation is involved in the equilibrium in the case of compound (XXVII).[113]



The fact that the *syn*-boat form obtains is readily understood from the standpoint of the orientation of the bonds (Fig. 3). According to a calculation[113], the contribution of the torsional interaction energy in the case of the half-chair and the *syn*-boat amounts to ~3 kcal mol^{-1}, while for the anti-boat form it is more than 7 kcal mol^{-1}.

The envelope or highly distorted half-chair conformation is typical for epoxycyclohexanones (XXVIII). If carbonyl groups have been introduced into both α-positions, as in compound (XXIX) then, compared with the chair form, the *syn*-boat form has a more favourable orientation of the dipoles and conditions for the conjugation of the carbonyl groups with the oxiran ring; ultimately, simple calculation predicts the highest stability of compound (XXIX) in the *syn*-boat form. Compound (XXX) has precisely this structure[114]. The substituent in the 1(6)-position is responsible for the "uneclipsed" half-chair conformation being preferred, as in bicycloheptanes (Fig. 3). This has been demonstrated in compound (XXXI) with R = H; however, when R = t-C_4H_9, the ring conformation is determined by the bulky substituent [115].

The orientation of the substituents in the other positions of 7-oxabicycloheptane is determined to a large extent by the direction of their dipoles relative to the epoxy-group. Apart from the general preference for the equatorial orientation, electrostatic repulsion destabilises the *cis*-axial positions of the polar substituents. It has been shown[110] that the *cis*- and *trans*-isomers of compound (XXXII, X = SO_2Ph, NO_2, or CN) exist preferentially in the equatorial form, but the fraction of the axial form of the *cis*-isomers is systematically lower, so that the values of ΔG for these compounds are smaller by 0.7 kcal mol^{-1} than for the *trans*-isomers[110,116];

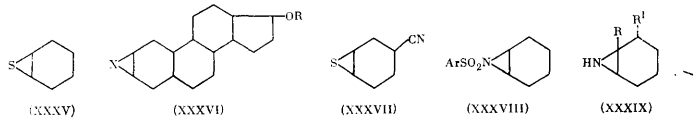


(XXXI) (XXXII) (XXXIII) (XXXIV)

the ratio of the values of ΔG mentioned above holds also for these compounds. Since the *cis*-substituent does not tend to occupy the axial position, the *trans*-3,4-dicyanides and the *trans*-3,4-diesters (XXXIII) exist preferentially in the *ee*-form[116,117].

The substituents in 2- and 5-positions to some extent retain the features of the conformational behaviour of cyclohexanes. This is indicated by the axial orientation of the 3-*cis*-t-butyl group in compound (XXXIV).[116] On the other hand, in general the ring conformation is determined mainly by the substituents in the 3,4- and not 2,5-positions (see, for example, Tadwalkar et al.,[118] Watanabe et al.,[119] and Jackson and Zurqiyah[120]).

The 7-heteroanalogues of bicycloheptane with other heteroatoms have been scarcely investigated. Cyclohexenothiiran (XXXV) has been found to have the half-chair conformation with the angle $\psi = 27.6°$.[121] A similar analogy with the corresponding epoxides has been observed in the structure of epithioandrostanes (XXXIV) with X = S (a) and SO (b).[122,123]



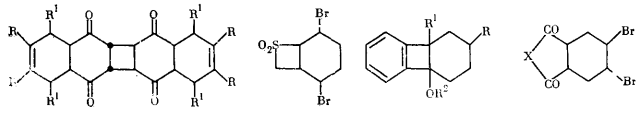
(XXXV) (XXXVI) (XXXVII) (XXXVIII) (XXXIX)

The *A* ring has the distorted half-chair conformation. The similarity of the dipole moment of cyanocyclohexenothiiran (XXXVII) to that of the epoxide has in fact led to the conclusion that the former is involved in an analogous conformational equilibrium with participation of about 40% of the equatorial half-chair conformation[48].

A typical half-chair conformation has been observed in an X-ray diffraction study of 7-(*p*-iodobenzenesulphonyl)-7-azabicyclo[4.1.0]heptane (XXXVIII).[124] Substituted compounds of type (XXXIX) have been investigated by ^{13}C NMR.[125] The substituent R^1 in the *trans*-position relative to the nitrogen atom is pseudoaxial, while that in the *cis*-position is pseudoequatorial, i.e. only one half-chair conformation with an uneclipsed substituent R is realised (Fig. 3).

3. Compounds of the Bicyclo[4.2.0]octane Series

A planar group arises only in the *cis*-condensation of the plane of the four-membered ring with the six-membered ring. Two groups of compounds have been investigated in fair detail. The first comprises the photodimers of hydrogenated naphthoquinones (XL).[126] The central four-membered rings in these compounds are planar and the cyclohexanedione rings have the half-chair conformation distorted to different extents, up to the envelope conformation, depending on the nature of the substituents R and R^1.



(XL) (XLI) (XLII) (XLIII)

The half-chair conformation has also been observed for compound (XLI); the C–Br bonds occupy the pseudoaxial positions, as in cyclohexene[127].

The compounds of the second group contain a six-membered ring condensed with the benzocyclobutene fragment, as in structure (XLII).[128,129] In all the molecules the cyclohexane ring has a fairly symmetrical boat conformation: the atoms in the 2- and 5-positions deviate from C(1)–C(3)–C(4)–C(6) by 0.55 and 0.62 Å respectively[128]. It is of interest that this is the *syn*-boat conformation, i.e. the bonds in the four-membered ring are axial.

4. The Anhydrides and Imides of *Cis*-cyclohexenedicarboxylic Acids

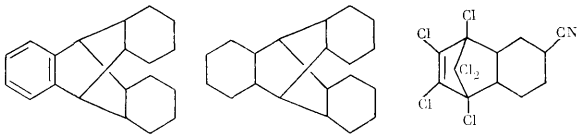
The tendency towards the formation of the boat form is manifested also in those cases where the cyclohexane ring is *cis*-condensed with a planar five-membered ring—anhydride or imide ring, as in compounds (XLIII, X = O or NAr). Compounds of this type have been investigated in solutions by various methods and it has been definitely established that there is an equilibrium between the diaxial half-chair and *syn*-boat conformations in proportions of 4 : 1 for anhydrides and 3 : 2 for *N*-arylimides[130].

The NMR spectra of the methyl-substituted anhydrides were interpreted as evidence for the twist-boat conformation; the possibility of an equilibrium was not taken into account[131].

5. The Cyclohexane Ring Condensed with a Bridged System

The limiting case in the series of bicyclo[4.*n*.0]alkanes considered consists of a cyclohexane ring *cis*-condensed with a similar ring incorporated in a rigid bicyclic system ensuring the coplanarity of the three consecutively arranged C–C bonds. A series of X-ray diffraction studies have been made of the possible isomers of the hydrogenated triptycenes (XLIV) and (XLV).[132–137]. All the *cis*-condensed rings have the boat conformation owing to the necessity for the optimum blending of the "rigid" and "mobile" halves of the ring.

When the contributions of different energy components are considered it is seen that the *cis,cis,cis*-form (three boats) involves a torsional energy loss of ~10 kcal mol^{-1} relative to the *trans,trans,trans*-form (three chairs), but there is a gain of the same amount of energy due to the Baeyer strain, since the overall destabilisation of the molecule in the "three boat" conformation does not exceed 2.5 kcal mol^{-1}.[136] The boat forms in compound (XLV) are somewhat distorted: the endocyclic dihedral angles formed by the common bond reach 17° for a very small inversion barrier between two directions of twist.



(XLIV) (XLV) (XLVI)

The observation of the stability of the boat conformation of the classical cyclohexane ring is an important achievement in the development of conformational analysis, because it necessitates a review of the structures of many compounds. It is appropriate to mention here that the preference for the boat conformation over the half-chair conformation has been demonstrated by calculations for the inversion of cyclohexane[138].

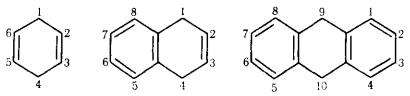
The C-C bonds in the bicyclic systems of compounds (XLIV) and (XLV) occupy an equatorial position in the cyclohexane ring, which is quite understandable from the standpoint of steric factors, although it conflicts with some of the data presented above for the bonds in three-, four-, and five-membered rings.

Substituted derivatives have been hardly investigated. The structure of the isomeric cyano- derivatives (XLVI) with the *cis*- and *trans*-dispositions of the cyano-group and the bicyclic system has been determined by the dipole moment method[139].

IV. 1,4-DIPLANAR SIX-MEMBERED RINGS

1. Aromatic 1,4-Dihydro-compounds

The series considered includes three main types of molecules—cyclohexa-1,4-diene (XLVII), 1,4-dihydronaphthalene (XLVIII), and 9,10-dihydroanthracene (XLIX).



(LXVII) (XLVIII) (XLIX)

The only possibility for a change in conformation involves the bending of the molecule along the C(1)-C(4)-C(9)-C(10) line, so that the ring always assumes the boat conformation specified by the angle θ between the planes of the π-electron systems (Fig.4).

(a) Cyclohexa-1,4-diene and its Derivatives

The planar structure of the molecule of compound (XLVII) is indicated by vibrational spectroscopy[140-143], rotational spectroscopy[144], gas phase electron diffraction[145], and NMR spectroscopy (in a nematic solvent)[146], the potential well being very flat[143], so that the effective angle θ is 167°.[147] This is apparently why it was concluded that the cyclohexa-1,4-diene molecule is non-planar[148]. Theoretical calculations by various methods confirmed the planar structure of compound (XLVII).[23,36,149-154]. Even though calculations indicated an energy barrier at θ = 180°, its height was found to be only ~0.1 kcal mol^{-1}.[155]

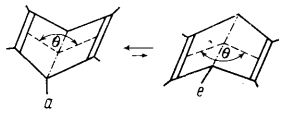
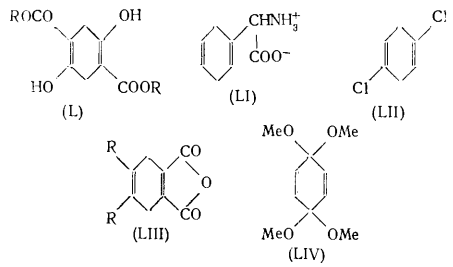


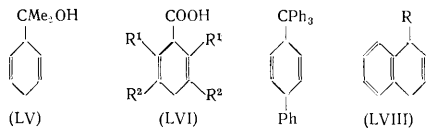
Figure 4. The structure of cyclohexa-1,4-diene and its derivatives.

Substituents at the olefinic atoms do not influence the ring conformation; this was established in an X-ray diffraction study of compounds (L) and (LI),[24,25] although the physical properties of solutions of compounds such as (LII) and (LIII) indicate an appreciable bending of the molecules, which may be effective[156,157]. The 1,1-disubstituted derivatives are also planar, since the bending increases the $A^{1,2}$ strain. An example may be provided by the diketal of the quinone (LIV).[158]



(L) (LI) (LII) (LIII) (LIV)

The conformations of 1-substituted cyclohexadienes are very interesting. When the substituents are not unduly bulky, the NMR spectra indicate the planarity of the ring[159-161]. With increase of the bulk of the substituent, there is an increase of the $A^{1,2}$ strain, so that a pseudoaxial boat conformation was observed for compound (LV).[162] The influence of the substituent on the ring conformation is reflected in the results of the calculation[150]: with increase of the bulk of the 1-substituent, the angle θ changes from 180° to 160° for t-butylcyclohexadiene; there are no energy minima at all corresponding to the pseudoequatorial orientations.



(LV) (LVI) (LVII) (LVIII)

The $A^{1,2}$ strain is equally enhanced after the introduction of substituents at the nearest sp^2-atoms.[163] In particular, in the molecule of compound (LVI), the ring is almost planar for $R^1 = H$ and $R^2 = Me$, but, when $R^1 = Me$ and $R^2 = H$, it is bent at an angle of 8.4°.[164]

1,4-Disubstituted derivatives with the *trans*-configuration have a planar ring (see the data published by Kitaigorodskii et al.[25]) or the more bulky substituent occupies the pseudo-axial position, as in compound (LVII).[165] It is of interest that the *cis*-isomer is diequatorial and not diaxial as might have been expected[166]: the deviation in the opposite direction would not alter appreciably the $A^{1,2}$ strain but would lead to the appearance of the prow-interaction.

(b) 1,4-Dihydronaphthalenes

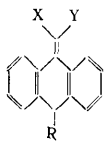
Condensation of cyclohexa-1,4-diene with an aromatic ring increases the $A^{1,2}$ strain and in addition there is a decrease in the torsional barriers in the $C_{sp^2}-C_{sp^3}$ bonds[23]; all this leads to an increase of conformational mobility. Although calculations, predicted a planar structure of compound (LVIII) for R = H,[150,151] experiment indicated a bend, albeit small, in the molecule[167]. Substituents in the 1-position are usually pseudoaxial[161,168-170]. The angle θ depends on the bulk of the substituent[171] and, in the presence of the bulky t-butyl substituent, there is a possibility that the ring form changes completely[172]; however, calculation for all the 1-alkyldihydronaphthalenes indicates the boat conformation with the sole difference that two energy minima correspond to the t-butyl group, with the corresponding angles θ = 132° (*e'*) and 149° (*a'*).[150]

(c) The 9,10-Dihydroanthracene System

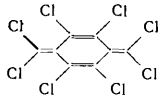
Numerous X-ray diffraction data indicate an appreciable bend in the molecules of 9,10-dihydroanthracene (XLIX) and its derivatives[24,25], which, incidentally, is poorly described by the theory[150,154]. For the two bonds in which the atom in the 9(10)-position is involved, that carrying the larger substituent is predominantly pseudoaxial[161,173] and there is a possibility of equilibrium between two forms[174]. The behaviour of 9-alkyldihydroanthracenes has been satisfactorily accounted for by calculation[150].

The *trans*-9,10-disubstituted dihydroanthracenes are largely planar, but, in the presence of very bulky substituents, there is a possibility of distortion of the ring[175]; naturally, if the substituents are different, the conformation is determined by the larger substituent. The central ring in symmetrical 9,9,10,10-tetrasubstituted compounds and compounds with condensed benzene rings is also planar[24]. The *cis*-configuration of the 9,10-substituents ensures the possibility of the energetically favourable diaxial conformation. Indeed, it has been observed for a number of dialkyl [25,175] and bis(trimethylsilyl)[176] derivatives. The angle θ is almost constant, varying in the range 150-155.7°. The same conformation is maintained in solutions[177].

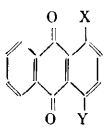
The sterically hindered molecules of type (LIX) with an sp^2-atom in the 9-position constitute a special group. An extremely pronounced 1,3-allylic ($A^{1,3}$) strain[1] between the substituents in the methylene group and the nearest hydrogen atoms of the hydroanthracene system is present in these compounds. The molecule therefore assumes that boat conformation, although sterically unhindered compounds of this type are planar[178]. The substituent R in the 10-position assumes the pseudoaxial orientation[179]. The $A^{1,3}$ interaction destabilises the planar structure so much that the height of the inversion barriers exceeds 15 kcal mol^{-1} [178-180] when X,Y ≠ H or for an unsubstituted methylene group and chlorine atoms in the 1- and 8-positions. Even in a quinonoid structure there is a possibility of the breakdown of planarity as a consequence of steric hindrance. Thus compound (LX) has a distinct boat conformation, in which the angle between the directions of the exocyclic double bonds is ~110°.[181]



(LIX)



(LX)



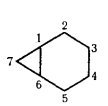
(LXI)

Even the molecules of aromatic compounds, for example, anthraquinones (LXI), can be non-planar as a result of steric hindrance. The bending of the ring requires at least two substituents in the 1,4- or 1,8-positions. For example, the 1,8-dichloroanthraquinone molecule is bent along the C(9)–C(10) line with θ = 168°.[182] The degree of non-coplanarity is still greater if X is a nitrogen atom incorporated in a 1,2-condensed aromatic heterocycle: the atoms in the 9- and 10-positions can be displaced from the plane by 0.2–0.4 Å [183,184].

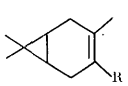
2. Bicyclo[4.1.0]hept-3-ene and Its Analogues

(a) Bicycloheptenes and Epoxycyclohexenes

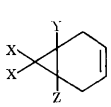
When the cyclohexene ring is condensed with a three-membered ring in the 4,5-positions, there is a possibility of two different boat conformations–*syn* and *anti* (Fig. 5). Bicyclo[4.1.0]hept-3-ene (norcarene) (LXII) and its homologues exist in the *syn*-boat form[185], like 3-carene (LXIII, R = H), whose structure has been determined most reliably by gas-phase electron diffraction[186], NMR spectroscopy[187,188], and the Kerr effect[189]. The angle θ is 165°.[82] The possibility of the involvement of the *anti*-form in the equilibrium in an amount of 5–10% ($\Delta G = 1.48$ kcal mol^{-1}) has been indicated[187]. The structure of 4-methylcarene (LXIII, R = Me) with θ = 172° is even closer to planarity[190]. Steric interactions have been suggested as a factor stabilising the *syn*-form[187], but calculations[189,191] have demonstrated that the torsional term plays the decisive role.



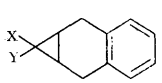
(LXII)



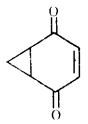
(LXIII)



(LXIV)



(LXV)

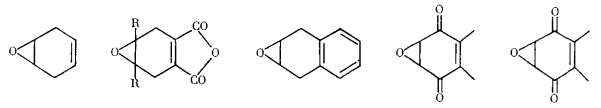


(LXVI)

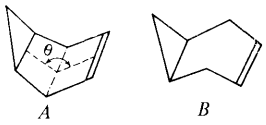
The data for norcarenes with polar substituents in the cyclopropane ring are contradictory. 7,7-Dihalogeno-derivatives exist in the *syn*-boat conformation with θ ≅ 165°.[192] The NMR spectra of the polyhalogeno-compounds (LXIV, X, Y, Z = F, Cl, or Br) indicate the *anti*-structure[193]. Just as contradictory results have been obtained for tetralin derivatives (LXV). If there is no substituent in the *syn*-7-position, the *syn*-boat conformation obtains[191,194]. However, the *anti*-structure with θ = 222° has been established with the aid of various methods for molecules with dichlorocyclopropane and dibromocyclopropane fragments[191,195].

The introduction of carbonyl groups in the 2,5-positions as in compound (LXVI) gives rise to the possibility of conjugation which flattens the ring. On the other hand, the torsional energy minimum retains its position, since the configuration with eclipsed carbonyl groups and C_{ring}–H bonds is favourable. The *syn*-conformations therefore obtain for compounds of type (LXVI) in crystals[24,25] and in solutions[196]. The angle of the bend remains the same as in analogues without carbonyl groups, so that the torsional term is decisive.

The oxygen analogue of norcarene-7-oxabicyclo[4.1.0]-hept-3-ene (LXVII)—has been investigated in fair detail in the gas phase[197,198]. The molecule has the *syn*-boat conformation with the angle $\theta = 160°$.[197] According to Durig et al.[198], the *anti*-boat conformation has an energy greater by 2.33 kcal mol^{-1}, i.e. is hardly involved in the equilibrium; the energy barrier separating the two forms is only 2.81 kcal mol^{-1}. Compound (LXVIII) has a fairly distinct *syn*-boat conformation, but its dipoles are directed to one side[157]. On passing to the tetralin analogue (LXIX), an inversion of conformation takes place, as for compound (LXV) and the *anti*-boat form with the same angle of bend of 219° becomes stable[196].



(LXVII) (LXVIII) (LXIX) (LXX) (LXXI)



A *B*

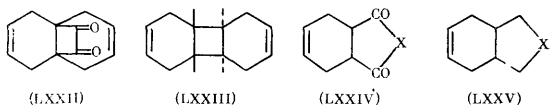
Figure 5. The possible conformation of bycyclo[4.1.0]-hept-3-enes; *A*—*syn*-form; *B*—*anti*-form.

Theoretical calculation[191] predicted the stability of the *anti*-boat form for the 7,7-dihalogeno-derivatives as a consequence of the repulsion of the π-electron systems and electron pairs of the *syn*-halogens. However, at the present time this conformation has been established reliably only for the benzo-derivatives, while the cyclohexene analogues (LXIV, Y = Z = H) and (LXVII) exist in the *syn*-form.

The introduction of carbonyl-containing groups stabilises additionally the *syn*-boat conformation not only as a result of the decrease of the torsional energy but also as a result of the most favourable orientations of the dipoles[199]. It is not surprising that this conformation is characteristic of epoxyquinones (LXX)[196,199] and hydroxyketones (LXXI).[24,200]

(b) Derivatives of Bicyclo[4.2.0]oct-3-ene

The planarity of the four-membered ring condensed with the cyclohexane ring, which is necessary for a fixation of all three bonds of the latter, is by no means always manifested; even the cyclobutene fragment is strongly bent in many instances[24]. The cyclobutane-1,2-dione ring is planar, as a result of which the molecule of compound (LXXII) exists in the crystal with the cyclohexene ring having the *syn*-boat conformation. The four-membered ring then occupies the axial position and the bonds in the second cyclohexene ring are equatorial[201]. Spectroscopic data[202] permit the same conclusion for solutions.



(LXXII) (LXXIII) (LXXIV) (LXXV)

The cyclobutane ring exhibits planarising properties in polycyclic molecules with the skeleton of compound (LXXIII) (but not in all cases)[25]. The degree of bending of the cyclohexene ring can be greater than in the bicycloheptene series—up to $\theta = 142°$.

(c) The Bicyclo[4.3.0]non-3-ene System

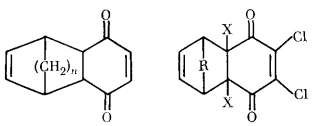
The five-membered anhydride and imide rings are planar in all cases, as a result of which the derivatives (LXXIV) exist in the boat conformation. The view has been frequently expressed that this is the *anti*-boat conformation, but experimental data have shown that the *syn*-form predominates ($n = 90 \pm 10\%$) for anhydrides[203,204], while the imides (LXXIV, X = NAr) exist as a mixture of approximately equal amounts of molecules in the *syn*- and *anti*-boat conformations[192].

Spectroscopic data on the basis of which the equilibrium in solutions might have been inferred unambiguously became available only recently and yielded ambiguous results. According to Larter et al.[205], the anhydride (LXXIV) and its homologues are equilibrium mixtures of the *syn*- and *anti*-forms in proportions of 9:1, in excellent agreement with other data[203]; the degree of bending of the ring was then assumed to be the same as that found in the X-ray diffraction study of cyclohexene *cis*-condensed with a five-membered ring[206]. The study of the temperature variation of the ^1H NMR spectra of compounds (LXXIV)[62] confirmed the *syn*-boat conformation at the usual temperatures, but characteristic signs of equilibrium were observed only on heating above 450 K, which should correspond to an unusually high barrier to inversion.

In the series of bicyclonon-3-enes the *cis*-junction between the cyclohexene ring and the saturated five-membered heterocycle is rigid, as in compound (LXXV). When $X = N^+Me_2$, the degree of bending is very marked: $\theta = 139.7°$.[206] The substance crystallises in the *anti*-boat form, although the *syn*-form is permissible in solution according to NMR data. The equilibrium has been studied in detail for X = O[207] and it has been established that the fraction of molecules in the *anti*-boat conformation is 60–80%.

(d) Adducts of Quinones with Cyclic Dienes

All the compounds investigated in which cyclohexene ring is *cis*-condensed with a bicyclic system can be obtained as adducts in the diene synthesis of *p*-quinones with cyclodienes. The cyclohexenedione ring in compound (LXXVI) with $n = 1, 2$ has the *syn*-boat conformation with an angle of bend close to the canonical value[114,208]: even bulky bicyclic systems can occupy the axial position.



(LXXVI) (LXXVII)

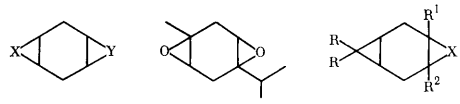
The same conformation has been established for adducts of quinones with hexachlorocyclopentadiene and even with anthracene, although in the latter case the ring is flattened[114,196]. The *syn*-boat conformation has been noted for quinoxalinedione adducts[209].

The adducts of substituted quinones of type (LXXVII) crystallise in the *syn*-boat form[210], but in solution there is a possibility of equilibrium, since in the boat form both the axial and equatorial positions are occupied by the C–C or C–X bonds[114].

3. 1,4-Diplanar Systems Formed by Condensation with Two Rings.

(a) Tricyclo[5.1.$0^{3,5}$]octanes

Mainly compounds (LXXVIII) with a *trans*-junction have been investigated, while only a few data have been obtained for the *cis*-isomers.



(LXXVIII) (LXXIX) (LXXX)

For the symmetrical derivatives (LXXVIII), the main problem was that of the degree of bending of the central ring. It was established ultimately that, for X = Y = CCl_2, CBr_2, or O,[211] and also for the *trans*-dioxide of γ-terpinene (LXXIX)[192], the angle θ between the C(1)–C(2)–C(5)–C(6) and C(2)–C(3)–C(4)–C(5) planes is ~160°. X-Ray diffraction study of compound (LXXX, R = R^1 = Me, R^2 = H, X = CBr_2) showed, however, that the degree of bending varies in the range 0.5–6.1°:[212] similarly, electron diffraction study of the analogous dichloride showed that it is best described by a planar structure[213]. Nevertheless, NMR study of compounds of type (LXXX) demonstrated in all cases the existence of conformational equilibria, which are possible only for a fairly high degree of bending of the molecules[214,215]. The determination of the structure of oxatricyclooctanes methylated to different extents (R = R^2 = H, R^1 = Me; R = H, R^1 = R^2 = Me;[216] R = R^1 = Me, R^2 = H;[217] R = R^1 = R^2 = Me)[187] showed that it depends on the degree of substitution, but the central ring is always significantly non-planar.

In the series of bicyclene oxides, X-ray diffraction data have been obtained for compound (LXXVIII, X = CBr_3, Y = O) and its 1,6-dimethyl derivatives[218]. Extremely small angles of bend of the ring were obtained—7.6° and 6.4° respectively. However, in solutions the polarity and polarisability of the *trans*-oxides of 7,7-dichloro-, and 7,7-dibromonorcarenes cannot be described in terms of a planar conformation; they can be treated only in terms of an equilibrium mixture of two boat forms[208]. The symmetrisation of molecules of this kind in the crystal is encountered fairly frequently.

According to electron diffraction data, the *trans*-oxide of 3-carene (LXXX, R = R^1 = Me, R^2 = H, X = O) has a pseudoaxial cyclopropane fragment and a pseudoequatorial epoxide ring (Fig.6, *syn*-boat)[219] with θ = 160°.[82] Studies in solutions by the NMR [220,222] and Kerr effect[223] methods revealed a conformational equilibrium in which the *syn*-boat form predominates (2:1).[223] The same ratio of conformers obtains for compound (LXXX, R = R^1 = Me, R^2 = COMe, X = O).[224] Equilibria in solutions have been discovered for a number of homologues of 3-carene oxide, the ratio of the conformers depending on the degree of methylation[190,225–227], and for 3-carene *trans*-sulphide (LXXX, R = R^1 = Me, R^2 = H, X = S)[228]. The only exception is a study[218] in which the NMR spectra of the *trans*-oxides of norcarene (LXXVIII, X = CH_2, Y = O) and its 7,7-dimethyl derivative were interpreted as evidence for the planar structure of the central ring.

The *cis*-isomers of compounds (LXXVIII) can exist in the *anti,anti*- or *syn-syn*-conformations (Fig.6), which are significantly different. The *anti,anti*-conformation is doubly destabilised by torsional interactons, while for the *syn,syn*-conformer one may expect stronger interactions between three-membered rings, particularly when these are polar or carry bulky substituents. Studies on the *cis*-oxide of 3-carene (LXXX, R = R^1 = Me, R^2 = H, X = O) by various methods revealed the presence of the *syn,syn*-boat form with θ = 160°,[219,223,229] as for its various homologues[226,227] and 3-carene *cis*-sulphide[228]. The dipole moment of the *cis*-dioxide of γ-terpinene (LXXIX) shows that the oxiran rings have a parallel or nearly parallel orientation, which is possible only for the *syn,syn*-boat conformation[192]. Only certain NMR studies led to the unambiguous conclusion that the *anti,anti*-form is possible or even more stable or that the planar structure obtains[218,221,222,225,228].

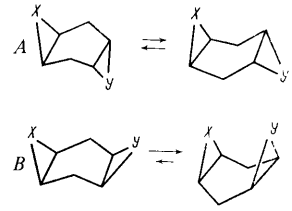
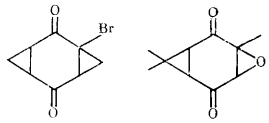


Figure 6. The conformations of 1,4-diplanar tricyclic systems with the *trans*-configuration (*A*) and the *cis*-configuration (*B*).

Ketones of the tricyclopropane series, investigated from the conformational standpoint, have the *trans*-disposition of two three-membered rings. The virtually symmetrical molecule of compound (LXXXI) has an almost planar six-membered ring in the crystal with θ = 175°.[230]



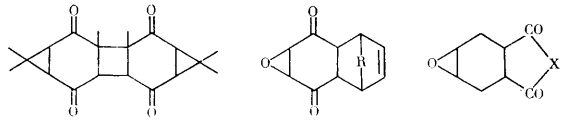
(LXXXI) (LXXXII)

If one of the rings is an epoxide ring, as in compound (LXXXII), it has a pseudoaxial orientation with favourable directions of the dipoles of the carbonyl groups and of the epoxide ring[196].

(b) Conformation of the Cyclohexane Ring in Certain Polycyclic Systems

The number of structures which can be formed on 1,4-condensation of the cyclohexane ring with various rigid fragments is very large; the available data concern only some types of compounds.

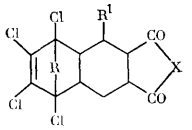
If one of the planarising fragments is a three-membered ring, it occupies the pseudoaxial position, i.e. in relation to this fragment the cyclohexane ring has the *syn*-boat conformation for reasons indicated above. Compound (LXXXIII) in the crystal[25] and the epoxy-derivatives (LXXXIV) in solutions[114,231] have such a structure. This angle of bend of the molecule of compound (LXXXIV) is approximately 150°.



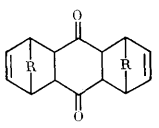
(LXXXIII) (LXXXIV) (LXXXV)

The epoxy-derivatives of the anhydrides and imides of cyclohexenedicarboxylic acids have the *cis*-configuration and exist in the *syn,syn*-boat form[192,203] like the *cis*-tricyclo-octane compounds, although the stabilising role of the torsional interactions is reduced by a factor of two compared with compound (LXXVII), while the electrostatic interactions are clearly unfavourable. These facts have no simple explanation and must be regarded as the manifestation of a specific conformational effect (the Pangolin effect).

In polycyclic anhydrides and imides of the type (LXXXVI, $R = CCl_2$ or CO, X = O or NAr, R^1 = H or Me) the cyclohexane ring has the *syn*-boat conformation in relation to the five-membered ring, so that the more bulky bridge system occupies the equatorial positions[232,233].



(LXXXVI)



(LXXXVII)

The exceptions to this rule are due to the equatorial location of the substituent R^1 *trans*-oriented relative to the five-membered ring.

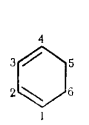
The bisadduct of quinone and cyclopentadiene (LXXXVII, $R = CH_2$)[234] and its tetrahydro-derivatives[235] have been investigated by X-ray diffraction. In the former case the carbonyl carbon atoms are displaced from the plane of the sp^3-atoms of the central ring by 0.37 Å, which corresponds to the classical boat conformation; a planar structure has been obtained by Norment[235]. This shows that small changes in the crystal lattice can give rise to a powerful conformational effect. In solutions the molecules have the boat conformation[208], which undergoes inversion at a high rate[236].

V. 1,3-DIPLANAR SYSTEMS

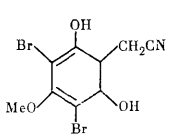
1. Cyclohexa-1,3-diene and Its Analogues

(a) The Ring Conformation

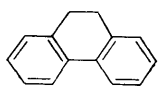
If two planar systems in the ring have a common bond, the only possibility for conformational movements is rotation about this bond [C(2)–C(3) in cyclohexa-1,3-diene (LXXXVIII)] until the distance between the C(5) and C(6) atoms becomes equal to the length of the C–C bond.



(LXXXVIII)



(LXXXIX)



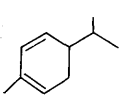
(XC)

In the molecule of compound (LXXXVIII) the angle ω between the planes of the double bonds is 17°,[237] 17.96°,[238] or 18.34°[148] according to electron diffraction data. A microwave study yielded 17.5°.[239] Spectroscopic data confirm the C_2 symmetry[142,240]. Two mirror-isomeric forms are separated by a fairly high inversion barrier, amounting to 3.15 kcal mol^{-1},[142] although a transition can be induced by rotation by only 35°. Theoretical calculations reproduce satisfactorily the height of the barrier and the positions of the potential energy minima (ω = 17–18°);[148,149,155] it is of interest that this angle has been obtained from the analysis of Dreiding models[241]. An X-ray diffraction study of compound (LXXXIX) yielded an angle of 17.3°;[242] in polycyclic systems the angle can diminish to 15° in steroids, 14° in glyotoxin, and 11.8° and 9.1° in laevopimaric acid[24,25].

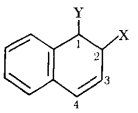
Calculation for the 9,10-dihydrophenanthrene fragment of compound (XC) yielded almost the same value as for cyclohexa-1,3-diene, namely ω = 15.3°.[243] The values of ω found for the crystalline phases of dihydrophenanthrenes[244,245], their benzo-derivatives[25], and their analogues with heteroaromatic rings[246,247] vary in the range 9.3–21°. Thus the cyclohexa-1,3-diene system exhibits a unique conformational constancy associated with the rigidity of its structure.

(b) The Conformation of the Substituents in the 5(6)-Positions

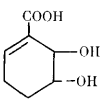
Since both sp^3-atoms are allylic, they are characterised by a pseudoaxial orientation of the substituents. Such orientation of the isopropyl group is in fact preferred for phellandrene (XCI):[248,249] $\Delta G = -0.42$ kcal mol^{-1}.[249]



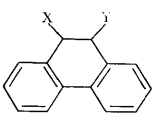
(XCI)



(XCII)



(XCIII)



(XCIV)

A comparison for a series of 5-alkyl derivatives has been carried out by an indirect method based on the ratio of the ring opening products; the pseudoaxial position was found to be energetically more favourable by an amount ranging from 0.24 kcal mol^{-1} for methyl to 2.98 kcal mol^{-1} for t-butyl[250]. The calculation[153] for the 5-methyl derivative predicted a greater stability of the pseudoequatorial form, but only to the extent of 0.025 kcal mol^{-1}. The two possible orientations of substituents such as the fluoro-, cyano-, and nitro-groups were also almost equivalent and the pseudoaxial position is appreciably preferred only for the hydroxyl and amino-groups: $\Delta G \cong -0.6$ kcal mol^{-1}.

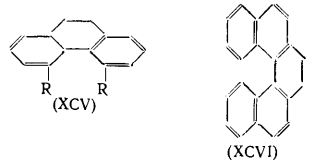
The substituents in the 2-position in the 1,2-dihydronaphthalene system (XCII, X = COR, Y = H) behave in the same manner: $\Delta G = -0.6 \pm 0.1$ kcal mol^{-1} for carbonyl functional groups, while for chlorine the two orientations are energetically equivalent[251]. On the other hand, the substituents in the benzyl 1-position in compound (XCII, X = H, Y = COR) are appreciably more axial[252,253] as a consequence of the $A^{1,3}$ strain. The *trans*-1,2-disubstituted dihydronaphthalenes are also preferentially diaxial and the introduction of a further substituent at the atom in the 8-position renders this form anancomeric [?enantiomeric][253–256]. The *trans*-5,6-derivatives of cyclohexa-1,3-diene have been scarcely investigated. It has only been observed that the conformational composition of dihydroxydihydrobenzoic acid (XCIII) varies sharply as a function of the solvent[257].

The substituents at the C_{sp^3} atoms of 9,10-dihydrophenanthrene (XCIV) are also preferentially pseudoaxial: the methyl, carbonyl, and dimethyl amino-groups are 75–80% pseudoaxial, and bulky substituents such as the t-butyl and trimethylsilyl groups are fully pseudoaxial; the cyano-group is as usual conformationally indifferent[258,259]. The *trans*-9,10-disubstituted derivatives are diaxial[258,260].

(c) Ring Inversion in 9,10-Dihydrophenanthrenes

Unsubstituted compounds with the cyclohexa-1,3-diene fragment have small inversion barriers[253], in agreement with calculation[261]. Their increase to a value measurable by NMR is acheived by the introduction of *cis*-substituents in the 9- and 10-positions in the dihydrophenanthrene

(XCIV) molecule[262], as in the cyclohexene series. The increase of steric hindrance in compounds of types (XCV) and (XCVI) gives rise to the possibility of the separation of the conformers, i.e. the barriers are more than 20 kcal mol^{-1}.



(XCV)

(XCVI)

The racemisation of bridged biphenyls has been the subject of numerous studies[259,263,264].

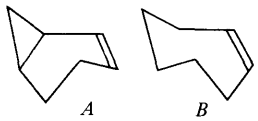


Figure 7. The relative positions of the bonds in the bicyclo[4.1.0]hept-2-ene molecule: *A*) *syn*-form; *B*) *anti*-form.

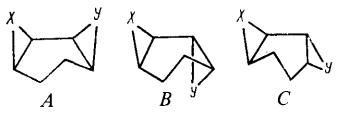
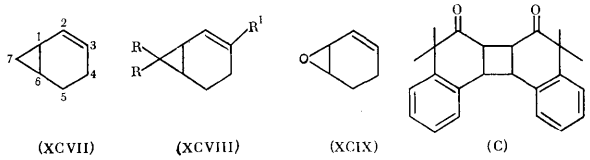


Figure 8. The steric structures of 1,3-diplanar compounds of the tricyclooctane series: *A*) *cis*-form; *B*) *trans,syn,syn*-form; *C*) *trans,anti,anti*-form.

2. The Bicyclo[4.1.0]hept-2-ene Series

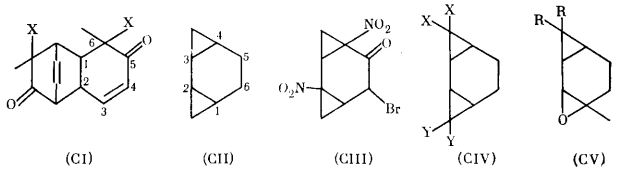
When a three-membered ring is introduced, two directions of the relative movement of the planar groups become non-equivalent. The atom in the 4-position in the (XCVII) system moves towards the three-membered ring (*syn*) or in the opposite direction (*anti*) (Fig.7). The study of compound (XCVII) by gas electron diffraction showed that the dihedral angle of the C(1)–C(2) bond is 15.4°, i.e. it hardly changes compared with cyclohexa-1,3-diene. The ratio of the *syn*- and *anti*-forms is 3:7. The *anti*-form has also been found for 2-carene (XCVIII; R = R^1 = Me) [265] and its 7,7-dihalogeno-derivatives with R = Cl or Br and R^1 = H. [266] The opposite conclusion concerning the stability of the *syn*-boat form has been reached on the basis of the NMR spectrum for R = H and R^1 = Me. [267]



(XCVII) (XCVIII) (XCIX) (C)

The internal rotation potential energy curve has been investigated for the 7-oxa-derivative (XCIX); [198] it has two minima with an energy difference of 1.09 kcal mol^{-1}, also in favour of the *anti*-form. The inversion barrier is the same as in cyclohexadiene (3.82 kcal mol^{-1}). The flattening of the ring has been observed in some derivatives[268].

The tetralin fragment in the molecule of compound (C) has an analogous *anti*-conformation[269]. Among the molecules containing the cyclohexane ring 1,3-condensed with a bicylic system, the keto-derivatives (CI) have been studied.



(CI) (CII) (CIII) (CIV) (CV)

According to the conjugation conditions, they exist in the envelope form with displacement of the C(6) atom from the plane of the ring by 0.70 ± 0.13 Å: [270] the isomer in which the attractive interactions stabilise the *syn*-conformation is an exception[271].

3. Tricyclo[5.1.0.0^{2,4}] Octane and Its Heteroanalogues

As for the 1,4-diplanar analogues, the conformational behaviour of the tricyclic compounds (XCII) depends on their configuration. As a result of the rotation about the C(2)–C(3) bond in the *cis*-isomer, one of the three-membered rings acquires an environment of the *syn*-type while the other acquires one of the *anti*-type (Fig.8). On the other hand, the two conformations of the *trans*-isomer differ. Electron diffraction study of the two isomers of compound (XCII) yielded the angles ω = 17.87–18.20° (*cis*-isomer) and 15.75–16.68° (*trans*-isomer). [272] The *trans*-isomer consists of a mixture of conformers, but, in contrast to compound (XCVII), the *syn,syn*-conformer proved to be more stable (87 ± 5%). Evidently, the direction of the bend in the 1,3-diplanar system depends on very fine structural details. Furthermore, the *syn,syn*-form has been discovered for compound (CIII). [24] The *syn*-orientation is impossible for a three-membered ring with large substituents and for this reason the *anti,anti*-form of all the compounds (CIV, X,Y = Cl, Br, or Me) is stable[266]. The *trans*-oxide of 2-carene (CV, R = Me) exists in the same form[265]. The removal of the *gem*-dimethyl group leads to inversion to the same *syn,syn*-form as for the *trans*-isomer of compound (CII), [226]

The *cis*-isomers have been scarcely investigated. In the *cis*-dioxides of the terpene series the angle ω = 15–16° is retained[25]. If the rings are different, as in the *cis*-oxide of 2-norcarene (CV, R = H), the *syn*-conformation relative to the oxygen atom, which has less stringent steric requirements than the methylene group, is the most stable[226,267].

---oOo---

The data examined show that six-membered carbon rings with planar groups of atoms are characterised by certain common features in their conformational behaviour despite the wide variety of their structures. These include the tendency of the cyclohexane ring to assume the boat conformation on condensation with rigid rings, which may be due to torsional or electrostatic factors, as in the *syn*-boat form of bicyclo[4.1.0]heptane systems, the steric interactions, as

in the *anti*-boat form of polysubstituted bicycloheptanes, and the ring closure conditions, as in perhydrotriptycenes. Next, it is necessary to note the relative stability of the axial and pseudoaxial positions of the substituents, including bonds belonging to planarising cyclic groups. The preferential pseudoaxial orientation of the condensed three-membered rings is responsible for the stability of the *syn*-conformers even in the presence of pronounced steric hindrance.

The extents to which the different types of compounds have been investigated from the conformational standpoint are by no means the same; in a number of instances it is still impossible to speak of rigorous rules. However, the interest aroused by the conformational studies in this field, including the analysis of the stereochemical reactions, gives rise to the hope that considerable advances will be achieved in the immediate future.

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P-Hetero-substituted Phosphorus Ylides

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The literature data on the methods of synthesis and properties of ylides containing various heteroatoms at the phosphorus atom in the P = C group are surveyed and described systematically.
The bibliography includes 134 references.

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I. INTRODUCTION

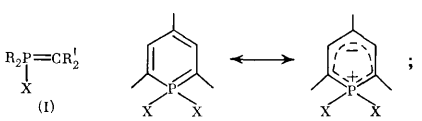
The interest in the chemistry of phosphorus ylides is due to the great theoretical and practical importance of these reactive compounds[1,2]. Phosphonium ylides are widely used in the laboratory and industrial Wittig synthesis of olefins and are employed in the synthesis of strained cycloalkanes, macrocyclic compounds, cyclic dienes and heavy metal complexes[3-10].

Structurally phosphorus ylides are carbanions stabilised by the neighbouring phosphonium group[1]:

$$R_3P{=}CR'_2 \longleftrightarrow R_3\overset{+}{P}{-}\overline{C}R'_2 .$$

The stability and reactivity of phosphorus ylides depend to a large extent on the substituents R' at the carbanionic centre. By varying these substituents, it is possible to obtain all possible types of *C*-substituted phosphorus ylides with exceptionally varied properties[1-10]. However, the substituents R at the phosphonium centre also exert a significant influence on the properties of ylides. Ylides containing heteroatoms attached to the phosphorus atom have especially interesting and frequently unusual properties; the chemistry of these compounds began to be investigated only in recent years. The principal results achieved in the synthesis and investigation of the properties of *P*-hetero-substituted phosphorus ylides (I) and published up to 1983 are the subject of the present review.

The review deals with acyclic *P*-hetero-substituted phosphorus ylides. Ylides containing a P=C bond in the ring, particularly λ^5-phosphorins, are not discussed in detail, since these compounds have specific chemical properties which resemble little those of acyclic phosphorus ylides:



(I)

X = Cl, Br, RS, R_2P, R_3Si, RO, HO, R_2N, RNH, H .

Electrophilic substitution reactions in the C(4)-position, comparable to the analogous reactions of other electron-enriched aromatic systems, for example, dimethylaniline, are characteristic of *P*-hetero-substituted λ^5-phosphorins. Their basicity and nucleophilicity are very low, they form stable radicals, give rise to stable π-complexes with heavy metal salts, etc.[11] Physicochemical studies confirming the unusual electronic structure of λ^5-phosphorins nevertheless make it possible to regard them as ylides in which the negative charge of the carbanionic component is delocalised over the ring[12,13].

II. METHODS OF SYNTHESIS

There exist several methods for the synthesis of *P*-hetero-substituted ylides. These compounds are usually obtained by the "oxidative ylidation" of phosphorus(III) compounds. The term "oxidative ylidation" implies reactions as a result of which the coordination number of the tervalent phosphorus atom increases and a P=C bond with a tetracoordinate phosphorus atom is formed[14]. Depending on the structure of the initial tervalent phosphorus compounds, their ylidation can proceed via two pathways: either a substituent X is introduced at the phosphorus atom of compound (II) with simultaneous deprotonation of the α-carbon atom or an alkylidene group is introduced in some way at the phosphorus atom of an X-substituted phosphine:

$$\underset{(II)}{R_2P{-}CHR'_2} \xrightarrow[-H^+]{[X]} \underset{(I)}{R_2P(X){=}CR'_2} \xleftarrow{I\diagdown\!\!\diagup CR'_2I} R_2PX .$$

The remaining methods of synthesis, especially the dehydrohalogenation of phosphonium salts and the conversion of one *P*-hetero-substituted phosphorus ylide into another, are used only in individual instances, but they sometimes have an advantage over "oxidative ylidation".

1. "Oxidative Ylidation" of Tervalent Phosphorus CH Acids

The "oxidative ylidation" of tertiary phosphines and phosphonites (II), containing a mobile hydrogen atom at the α-carbon atom and behaving as CH acids of tervalent phosphorus, must be regarded as the most flexible and general approach to the synthesis of *P*-hetero-substituted ylides[14-16]. Compounds (II) containing at the α-carbon atom only electron-accepting substituents R', enhancing the mobility of the hydrogen atoms and stabilising the ylide function, are ylidated most readily. However, in many instances it is possible to ylidate successfully also weak CH acids, such as, for example, trialkylphosphines. The phosphorus(III) CH acids are carbon analogues of the phosphorus(III) OH acids[14-20] and can be converted into ylides in the same way as the OH acids of tervalent phosphorus form compounds with a P=O group. In particular, the phosphorus(III) CH acids undergo reactions resembling the Atherton–Todd, Michaelis–Becker, etc. reactions characteristic of dialkyl phosphites. Certain alkylphosphines of type (II) isomerise to ylides with a P–H bond, analogous to the prototropic P(O)H forms of the phosphorus(III) OH acids, which emphasises still further the similarity of these types of organophosphorus compounds[18]:

$$R_2P{-}CHR'_2 \rightleftarrows R_2P(H){=}CR'_2 \quad R_2P{-}OH \rightleftarrows R_2P(H){=}O .$$

(a) Reactions of Compound (II) with Carbon Tetrahalides

Tertiary phosphines and phosphonites (II) containing electron-accepting substituents at the α-carbon atom are ylidated on interaction with carbon tetrachloride and alkylamines, aniline, or ammonia[15,16,19-22]. The reaction models the Atherton–Todd reaction, according to which dialkyl phosphites react with CCl_4 and alkylamines to form phosphoric acid amides[23]. The interaction of compound (II) with CCl_4 and alkylamines and also ammonia proceeds readily in ether at 0 °C, but the reaction with aniline must be carried out, in view of the low basicity of the latter, in the presence of triethylamine. The method employs readily available starting materials and makes it possible to vary widely the substituents at the phosphorus and carbon atoms of the P=C group:

$$R_2P{-}CHR'_2 \xrightarrow[-CHCl_3,\ -R''_2NH\cdot HCl]{CCl_4+R''_2NH} R_2P(NR''_2){=}CR'_2 \quad ;$$

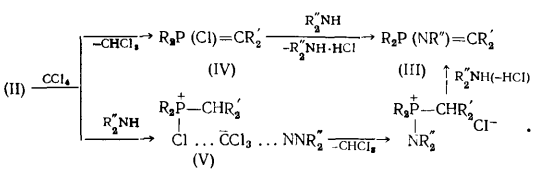
(II) (III), (50–70%)

R = Et, iso-Pr, Ph, EtO, iso-PrO; CR'_2 = $CHCO_2Et$, $CPhCO_2Me$, $C(CO_2Me)_2$, $CHSO_2CF_3$, $C(SO_2Ph)_2$; NR''_2 = NH_2, NHMe, NHPr-iso, NMe_2, NEt_2 ;

$$(iso\text{-}PrO)_2P{-}CH(CO_2Et)_2 \xrightarrow[-CHCl_3,\ -Et_3N\cdot HCl]{CCl_4+PhNH_2+Et_3N} (iso\text{-}PrO)_2P(PhNH){=}C(CO_2Et)_2 \ .$$

Compounds (II) are converted into ylides (III) via the intermediate formation of *P*-halogenoylides (IV)[15,20] or via the complex (V)[21]. Depending on the reaction conditions, the first or second pathway is followed (Scheme 1).

Scheme 1



In the absence of amines, compounds (II) react with $CHal_4$ to form ylides with a halogen atom attached to the phosphorus atom[14,16,24-30]:

$$R_2P{-}CHR'_2 + CHal_4 \rightarrow R_2P(Hal){=}CR'_2 + CHHal_3 \ ;$$

(II) (VI)

R = Et, iso-Pr, t-Bu, Ph, EtO, iso-PrO, Me_2N, Et_2N;

CR'_2 = CH_2, CHMe, CHPr, CHPr-iso, $CHSiMe_3$, CHSMe, CPh_2, fluorenylidene, cyclopentadienylidene, $C(SiMe_3)_2$, $CPhSiMe_3$, $C(CO_2Me)_2$, $C(CO_2Et)_2$, $C(SO_2Ph)_2$, $CHSO_2CF_3$;

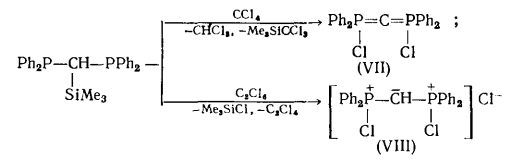
Hal = Cl, Br

The interaction of trialkylphosphines with carbon tetrachloride takes place readily on cooling to a temperature below 0 °C; less nucleophilic phosphonites react with carbon tetrachloride and are converted into *P*-chloroylides at an appreciable rate only in the presence of triethylamine, which exhibits a catalytic activity[14]:

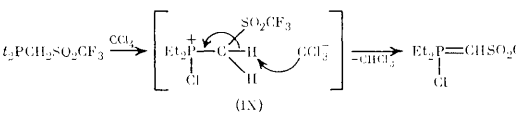
$$(EtO)_2P{-}CH(CO_2Et)_2 \underset{+H^+}{\overset{B,\ -H^+}{\rightleftharpoons}} \left[(EtO)_2P{-}\bar{C}(CO_2Et)_2 \rightleftharpoons (EtO)_2\bar{P}{=}C(CO_2Et)_2\right] \xrightarrow[-CHCl_3]{CCl_4} (EtO)_2P(Cl){=}C(CO_2Et)_2 \ .$$

However, phosphonites react with the very reactive carbon tetrabromide to form *P*-bromoylides even in the absence of triethylamine at −70 °C.[14] The yields of *P*-halogenoylides (VI) are usually high.

Interesting possibilities appear after the introduction of the trimethylsilyl group at the α-carbon atom in compound (II). Thus trimethylsilylbis(diphenylphosphino)methane gives rise to carbodiphosphorane (VII) on interaction with carbon tetrachloride as a result of the elimination of tribromotrimethylsilylethane and chloroform, while the reaction with hexachloroethane results in the formation of the ylide (VIII)[31,32]:



Compounds (II) are converted into *P*-halogenoylides owing to the presence of a mobile hydrogen atom at the α-carbon atom, as a result of which the anion $CHal_3^-$ readily deprotonates the quasi-phosphonium salt (IX) formed in the intermediate stage. Electron-accepting substituents at the α-carbon atom, which increase the mobility of the hydrogen atom, promote the formation of *P*-halogenoylides[14]:



However, weak CH acids such as trialkylphosphines can also be converted into *P*-halogenoylides, provided that there are bulky substituents at the phosphorus atom[28,29]:

$$t\text{-}Bu(R)PCH_2R' \xrightarrow[-CHHal_3]{CHal_4} t\text{-}Bu(R)P(Hal){=}CHR' \ ;$$

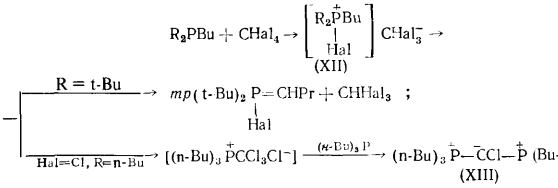
(X) (XI)

R = t-Bu, n-Bu, Et_2N, Me_2N; R′ = H, Me, n-Pr, iso-Pr; Hal = Cl, Br .

The "unstabilised" *P*-halogenoylides (XI) formed under these conditions are extremely reactive and are used for the synthesis of many interesting organophosphorus compounds.

Sterically unhindered tertiary phosphines, for example Me_3P or $n\text{-}Bu_3P$, do not form *P*-chlorides on interaction with CCl_4 but give rise to phosphoranylphosphonium salts (XIII)[33]. On the other hand, tertiary phosphines containing the t-butyl group are converted quantitatively into *P*-halogenoylides on interaction with carbon tetrahalides[28]. The influence of the steric shielding of the phosphorus atom on the pathway followed in the reactions of tertiary phosphines with carbon tetrahalides can be accounted for by Scheme 2 below:

Scheme 2



The interaction of a tertiary phosphine with $CHal_4$ results in the formation of the ion pair (XII), whose further reaction can proceed via two pathways: via the nucleophilic attack by $CHal_3^-$ on the phosphonium cation (anion exchange) or via the deprotonation of the α-carbon atom. The steric hindrance at the phosphorus atom generated by the t-butyl group is an obstacle to the interaction of $CHal_3^-$ with the phosphonium cation, as a consequence of which the deprotonation of the α-carbon atom becomes the dominant process. The mechanism has been confirmed by experimental observations[28].

The interaction of sterically hindered tertiary phosphines with carbon tetrabromide at −120 °C results in the formation of bright orange solid substances–bromophosphonium tribromomethanides (XIV)[28]. They exist at a very low temperature and, on increasing the latter to −90°– −60 °C, they are converted quantitatively into *P*-bromoylides. The stability of these unusual compounds is undoubtedly determined by the steric influence of the t-butyl groups at the phosphonium cation. Ion pairs of this type are also formed on interaction of sterically unhindered tertiary phosphines with carbon tetrahalides. However, in this case they behave as short-lived intermediates and can be "captured" by the proton-donating reagents only at the instant of their formation[34].

A conclusion concerning the structure of bromophosphonium tribromomethanides was reached on the basis of the study of their chemical reactions[28]. The reactions with deuterium chloride and chlorotrimethylsilane convincingly demonstrate the presence of the CBr_3^- anion:

$$(t\text{-Bu})_2PR + CBr_4 \xrightarrow{-120^\circ} (t\text{-Bu})_2\overset{+}{P}(Br)RCBr_3^- \ ;$$

R = t-Bu, n-Bu, Et_2N (XIV)

$$(XIV) \xrightarrow{-60^\circ,\ R=n\text{-Bu}} (t\text{-Bu})_2P(Br)=CHPr + CHBr_3 \ ;$$

$$(XIV) \xrightarrow{-120^\circ,\ DCl} (t\text{-Bu})_2(R)\overset{+}{P}ClBr^- + CDBr_3 \ ;$$

$$(XIV) \xrightarrow{-120^\circ,\ Me_3SiCl} (t\text{-Bu})_2(R)\overset{+}{P}ClBr^- + Me_3SiCBr_3 \ .$$

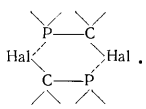
(b) The α-Halogenoalkylphosphine–P-Halogenoylide Rearrangement

The α-halogenoalkylphosphines (XV), formed on interaction of phosphinochloridous acids with halogenosulphonylmethanes, readily rearrange to *P*-halogenoylides (VI)[21,35]:

$$R_2PCl \xrightarrow[Na^+[HalCR'_2]^-]{HalCHR'_2+Et_3N} R_2P{-}\underset{(XV)}{CR'_2}{-}Hal \rightarrow \underset{(VI)}{R_2P(Hal)=CR'_2} \ ;$$

R = Et, iso-Pr, Ph; $CR'_2 = CHSO_2CF_3$, $C(SO_2Ph)_2$; Hal = Cl, Br .

The migration of the halogen atom from the α-carbon atom to the phosphorus atom (the C → P halogenotropic shift) increases the coordination number of the phosphorus atom and results in the formation of a P=C bond, i.e. "oxidative ylidation" takes place. The α-halogenoalkylphosphine (XV) contains a "positively charged" halogen to which the nucleophilic attack by the tervalent phosphorus atom may be directed, resulting in the abstraction of the halogen from the carbon atom. It is entirely likely that the transfer of the halogen from the carbon atom to the phosphorus atom proceeds via a six-membered transition state:



Electron-accepting substituents at the phosphorus atom, particularly halogen atoms, which make it less nucleophilic, prevent the rearrangement[36]:

$$Cl_3P + ClCH(CO_2Et)_2 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} Cl_2P{-}\underset{Cl}{C}(CO_2Et)_2 \not\rightarrow Cl_3P{=}C(CO_2Et)_2 \ .$$

The α-halogenoalkylphosphine–*P*-halogenoylide rearrangement was first observed in a number of compounds containing sulphonyl groups at the α-carbon atom[21,35]. However, it was shown subsequently that certain silicon-containing α-chloroalkylphosphines also readily rearrange to *P*-chloroylides[37,38]:

$$Me_2PLi + Cl_2C(SiCl_3)_2 \rightarrow Me_2P{-}\underset{Cl}{C}(SiCl_3)_2 \rightarrow Me_2P{=}\underset{Cl}{C}(SiCl_3)_2 \ ;$$

$$R_2PCl + LiClC(SiMe_3)_2 \rightarrow R_2P{-}\underset{Cl}{C}(SiMe_3)_2 \rightarrow R_2P{=}\underset{Cl}{C}(SiMe_3)_2 \ ;$$

R = Ph, Me_2N .

(c) Disproportionation of Tertiary Phosphines with a Mobile Hydrogen Atom at the α-Carbon Atom

Tervalent phosphorus compounds with a mobile hydrogen atom at the α-carbon atom exhibit a distinct tendency to be converted into phosphorus ylides. Thus diethylbis(alkoxycarbonyl)methylphosphines and diethyltrifluoromethanesulphonylmethylphosphine disproportionate on heating with formation of the ylides (XVII) containing a phosphorus–phosphorus bond[14,39]:

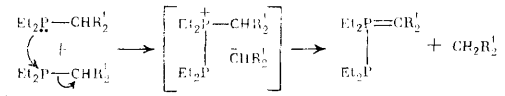
$$\underset{(XVI)}{2Et_2P{-}CHR'_2} \xrightarrow{120^\circ} \underset{(XVII)}{Et_2P{-}PEt_2{=}CR'_2} + CH_2R'_2 \ ;$$

$CR'_2 = CHSO_2CF_3$, $C(CO_2Me)_2$, $C(CO_2Et)_2$.

The disproportionation of compounds (XVI) is a reversible process. On heating with the simultaneous removal from the reaction sphere of the non-phosphorylated component $CH_2R'_2$, the equilibrium is fully displaced in the direction of the P–P ylides (XVII). Without heating and the removal of $CH_2R'_2$, the disproportionation of compounds (XVI) does not take place.

Scheme 3, taking into account the high lability of the P–P bond in compounds (XVI), explains the formation of P–P ylides (XVII).

Scheme 3



This lability is due to the effective stabilisation by the electron-accepting substituents R', formed on dissociation of the P–C bond of the carbanion CHR'_2, which becomes capable of playing the role of a readily eliminated group. Compounds (XVI) are cleaved at the P–C bond by alcohols, water, ketoenols, thiols, etc.[14]

The structure of the P–P ylides (XVII) is confirmed by spectroscopic data. The ^{31}P NMR spectra of the ylides (XVII) contain a double doublet of signals due to the tricoordinate and tetracoordinate phosphorus atoms. The constant $^1J_{PP}$ = 270–280 Hz corresponds to the spin–spin coupling of the phosphorus nuclei in the tetracoordinate phosphorus–tricoordinate phosphorus bond.

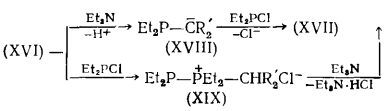
(d) Reactions of Tervalent Phosphorus CH Acids and Their Carbanions with Chlorine-containing Electrophiles

Tervalent phosphorus compounds (XVI) containing a mobile hydrogen atom at the α-carbon atoms form P–P ylides (XVII) also on interaction with chlorodiethylphosphine in the presence of triethylamine[14,20,40]. The reaction is carried out in ether at 0–10 °C:

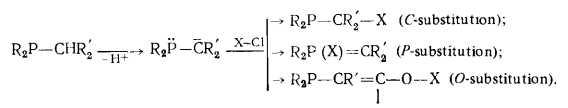
$$(XVI) + Et_2PCl \xrightarrow[-Et_3N\cdot HCl]{Et_3N} (XVII) \ .$$

A convenient method of synthesis of the P–P ylides (XVII) involves the reaction of malonic ester or trifluoromethanesulphonylmethane with two equivalents of chlorodiethylphosphine in the presence of an excess of triethylamine[14,39]. The tertiary phosphines (XVI), formed in the intermediate stage, can be obtained in high yields when the starting reactants are taken in proportions of 1:1.[14,25,40,41]

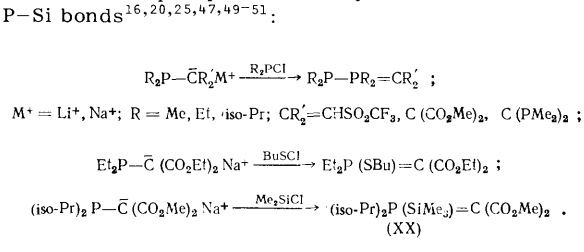
The P–P ylides (XVII) are apparently formed as a result of the *P*-phosphorylation of the α-phosphinocarbanion (XVIII) However, one cannot rule out also the electrophilic attack by chlorodiethylphosphine on the tervalent phosphorus atom of the tertiary phosphine (XVI) with subsequent dehydrochlorination of the phosphonium salt (XIX) (formed under these conditions) under the influence of triethylamine:



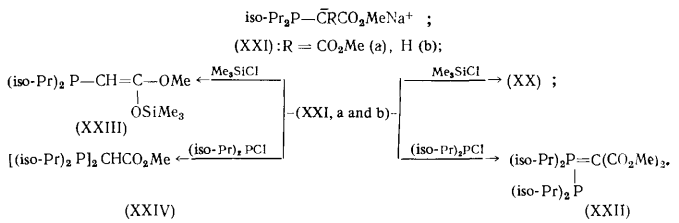
The α-phosphinocarbanions (XVIII), which are obtained by deprotonating alkylphosphines by various bases [lithium alkyls[20,42–45], sodium bis(trimethylsilyl)amide[46], sodium hydride[47], and even alkylamines[48]], can be converted in many instances into *P*-hetero-substituted phosphorus ylides. In principle, α-phosphinocarbanions can react with chlorine-containing electrophiles to form products substituted both at the carbon atom and at the phosphorus atom and, when the C=O group is present at the carbanionic centre, also products substituted at the oxygen atom:



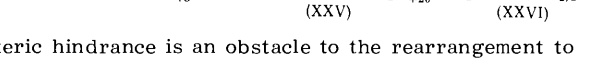
The mode of reaction of ambident α-phosphinocarbanions with chlorine-containing electrophiles (alkyl halides, tervalent phosphorus chlorides, sulphene chlorides, and chlorotrimethylsilane) is determined by kinetic and thermodynamic factors and depends primarily on the structure of the initial reactants. The presence of the electron-accepting groups CO_2R, SO_2R, and Me_2P at the α-carbon atom stabilises the ylide functional group, favouring the formation of products substituted at the phosphorus atom—ylides with P–P, P–S, and P–Si bonds[16,20,25,47,49–51]:



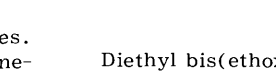
The influence of electron-accepting groups with substituents on the mode of reaction of α-phosphinocarbanions with chlorine-containing electrophiles is demonstrated by the following example. The carbanion (XXIa), containing two methoxycarbonyl groups, reacts with iso-Pr_2PCl and Me_3SiCl to form the ylides (XX) and (XXII)[47], while the carbanion (XXIb), with a single methoxycarbonyl group, gives rise to only the products (XXIII) and (XXIV) substituted at the C and O atoms[52]. The stabilisation of the *P*-substitution products by only one MeO_2C group in the latter case is insufficient:



When bis(diphenylphosphino)methyl-lithium reacts with chlorodialkylphosphines at −78 °C, a P–P ylide (XXV) is formed and, on raising the temperature to 20 °C, rearranges to triphosphinomethane (XXVI)[49]. Evidently, under the conditions of kinetic control, the less stable *P*-substitution product is formed and is then converted into the thermodynamically more favourable *C*-substitution product:

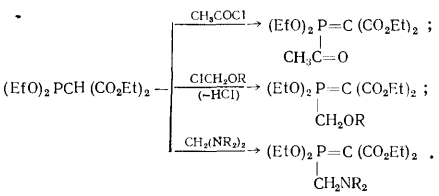


Steric hindrance is an obstacle to the rearrangement to triphosphinomethane, as a result of which the P–P ylide (XXVII) is isolated in a pure state[49]:



Diethyl bis(ethoxycarbonyl)methylphosphonite readily forms ylides by interaction with acetyl chloride in the presence of bases[53,54], with α-chloroethers under the conditions of the Arbuzov reaction[55], and also with aminomethylenes under the conditions of the Kabachnik–Fields reaction[56] (Scheme 4):

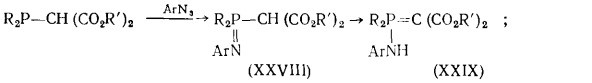
Scheme 4



(e) Prototropic Transformations of Phosphorylated CH Acids

The use of tervalent phosphorus compounds containing a mobile hydrogen atom at the α-carbon atom makes it possible to realise the extensive possibilities for their conversion into ylides as a result of reactions involving prototropic rearrangements.

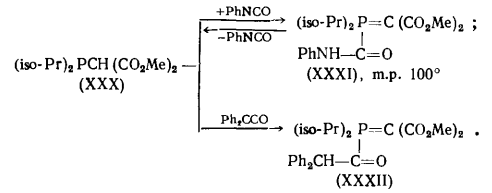
The Staudinger imination of bis(alkoxycarbonyl)methylphosphines and the analogous phosphonites by aryl azides yields the phosphazo-compounds (XXVIII), which readily rearrange to the ylides (XXIX) with the RNH group at the phosphorus atom[41,57–59] (for the phosphazo-ylide tautomerism, see Section III.4):



The driving force of this rearrangement is the endeavour by the system to form the least "acid" tautomeric form.

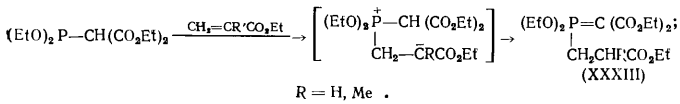
Phenyl isocyanate and diphenylketen readily add to the tertiary phosphine (XXX). The reaction proceeds with formation of the *P*-acyl-substituted ylides (XXXI) and

(XXXII)[25]:



The ylide (XXXI) is stable in the crystalline state, but in solutions it dissociates into the initial compounds. On cooling or removal of the solvent, the ylide (XXXI) is recovered from the solution in the crystalline form.

Diethyl bis(ethoxycarbonyl)methylphosphonite reacts with acrylic and methacrylic acid esters under the conditions of the Pudovik reaction with formation of the ylides (XXXIII)[60]:



It has been noted that in the presence of alkaline catalysts the yields of the ylides increase and the reaction is accelerated.

2. Introduction of an Alkylidene Group into Tervalent Phosphorus Compounds

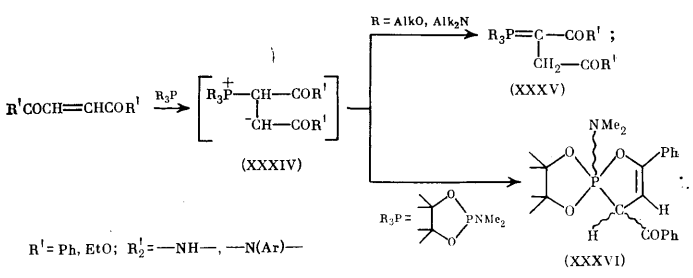
P-Hetero-substituted phosphorus ylides are formed when tervalent phosphorus acid derivatives interact with various compounds serving as sources of a substituted methylene fragment. Such sources can be carbenes, carbenoids, and various compounds with activated multiple bonds.

(a) Reactions of Tervalent Phosphorus Compounds with Alkenes and Alkynes

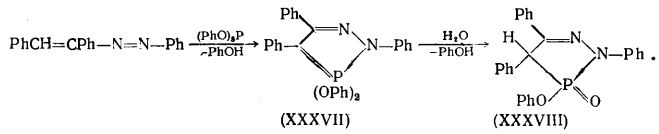
Compounds with an activated multiple bond readily react with tervalent phosphorus compounds and give rise to phosphorus ylides in many instances. Nucleophilic attack by the tervalent phosphorus atom on the electron-unsaturated carbon atom in the activated double bond produces a very reactive betaine (XXXIV), which readily rearranges to an ylide. An adequate mobility of the α-hydrogen atom is a condition which must be fulfilled for such a rearrangement. In the presence of the electron-accepting carbonyl group, the rearrangement of the betaine (XXXIV) to its less "acid" prototropic form, namely the ylide (XXXV), takes place readily. Thus the amides and esters of tervalent phosphorus acids add to maleimides[61-63], fumaric acid esters[64], and *trans*-dibenzoylethylene[65] with formation of the ylides (XXXV).

However, the presence of the five-membered dioxaphospholan ring favours the cyclisation of the betaine (XXXIV) to the phosphorane (XXXVI)[64] (Scheme 5).

Scheme 5

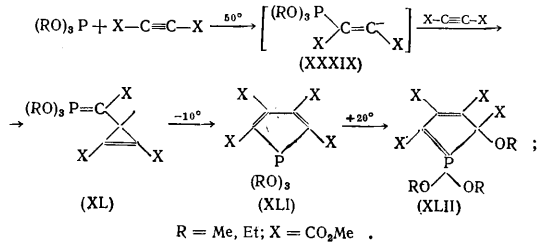


The ylides (XXXVII) with phenoxy-groups at the phosphorus atom have been obtained as a result of the [1 + 4]-cycloaddition of triphenyl phosphite to a conjugated azoalkene[66]. The chemical shift $\delta p = +43.7$ p.p.m. rules out a structure of the compound with a pentacoordinate phosphorus. The ylide (XXXVII) is very hygroscopic and is formed as a colourless solid product only after the complete removal of traces of moisture from the reaction mixture. In the presence of moisture, the ylide is instantly converted into the diazophosphole (XXXVIII):



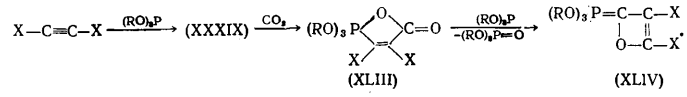
The reactions of acetylenedicarboxylic acid derivatives with tervalent phosphorus esters and amides proceeds in an interesting fashion. Thus the interaction of the methyl ester of this acid with trialkyl phosphites leads to the formation of the cyclic ylides (XLII) containing alkoxy-groups at the phosphorus atom[67,68]. NMR study of the reaction at a low temperature showed that the betaine (XXXIX) is formed initially and then its interaction with a second acetylenedicarboxylate molecule gives rise to the ylide (XL) with the cyclopropenyl group at the α-carbon atom. This ylide exists at −50 °C but, on raising the temperature to −10 °C, rearranges to the phosphorane (XLI), whose structure has been confirmed by the ^{31}P NMR spectrum ($\delta p = -37.4$ p.p.m.). At 20 °C the phosphorane is converted into the cyclic ylide (XLII)[67,68] via Scheme 6.

Scheme 6



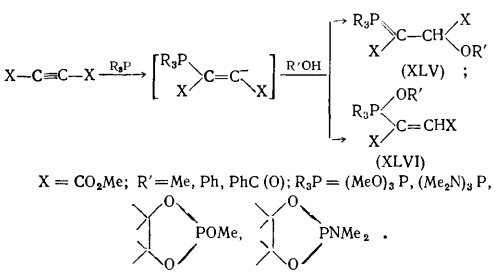
The ylides (XLII) have been obtained in the form of a crystalline substance and their structure has been convincingly confirmed by spectroscopic studies.

The betaine (XXXIX) interacts with carbon dioxide to form the phosphorane (XLIII) ($\delta p = -53.8$ p.p.m.), which is stable at a low temperature, but at 20 °C reacts with a second trialkyl phosphite molecule, gives up an oxygen atom to the latter, and is converted into the ylide (XLIV)[69]:



In the presence of hydroxylated reagents, the reaction of acetylenedicarboxylate ester with phosphites leads to the formation of ylides or phosphoranes. Acyclic phosphites give rise to the ylides (XLV), while five-membered cyclic phosphites yield the phosphoranes (XLVI)[70-72] (Scheme 7):

Scheme 7



(XLVI)

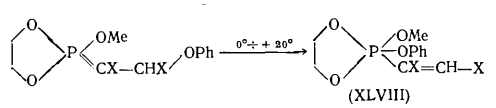
$X = CO_2Me$; $R' = Me$, Ph, PhC (O); $R_3P = (MeO)_3P$, $(Me_2N)_3P$,

Interesting transitions between the ylide and phosphorane structures, whose direction depends on the substituent R at the phosphorus atom and on the nature of the proton-donating reagent, have been observed with the aid of ^{31}P NMR. The rearrangement of the ylide to the phosphorane was observed in the interaction of trimethyl phosphite with acetylenedicarboxylate ester in the presence of a "trapping reagent"–methanol. At −40 °C the phosphorane can be detected in the reaction mixture, while at 20 °C it is converted into the ylide[73]:

$$(MeO)_4P{-}CX{=}CHX \xrightarrow{+20^\circ} (MeO)_3P{=}CX{-}CH\langle^{X}_{OMe} \quad .$$

(XLVII)

Conversely the reaction of acetylenedicarboxylate with cyclic phosphites and phenol at a low temperature gives rise to an ylide, which rearranges to the phosphorane (XLVIII) above 0 °C:



(XLVIII)

(b) Other Methods for the Introduction of the Methylene Group into Tervalent Phosphorus Compounds

A unique example of the synthesis of the ethoxycarbonyl ylide (XLIX) by displacing trimethylamine by an aminophosphine from a quaternary ammonium salt has been described[74]:

$$(Me_2N)_2PPh + Me_3\overset{+}{N}CH_2CO_2Et\ Cl^- \xrightarrow[-Me_3N\cdot HCl]{} (Me_2N)_2P{=}CHCO_2Et \quad .$$

Ph

(XLIX)

The formation of the trimethoxyphosphonium ylide (L) as a result of the interaction of tri(phenylthio)methyl-lithium with trimethyl phosphite has been reported[75]. The ylide (L) could not be isolated in a pure state, but its formation was demonstrated with the aid of the Wittig reaction. Under analogous conditions, the triphenylphosphonium ylide (LI) was obtained in the form of a pure crystalline substance:

$$(PhS)_3CLi + P(OMe)_3 \xrightarrow{-PhSLi} [(MeO)_3P{=}C(SPh)_2] \xrightarrow[-(MeO)_3P=O]{p\text{-}O_2NC_6H_4CHO}$$

(L)

$$\rightarrow p\text{-}O_2NC_6H_4CH{=}C(SPh)_2 \quad Ph_3P{=}C(SPh)_2 \quad .$$

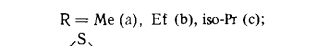
(LI)

Compounds of tervalent phosphorus react with certain thioketones and their dimers to form the ylides (LII). The formation of a carbene in an intermediate stage, which then reacts with the second phosphite molecule, has been postulated. The ylides (LII) are stable liquids which can be vacuum-distilled[76]:

$$(CF_3)_2C{=}S + P(OR)_3 \xrightarrow{-(RO)_3P=S} [(CF_3)_2C{:}] \xrightarrow{P(OR)_3} (RO)_3P{=}C(CF_3)_2 \ ;$$

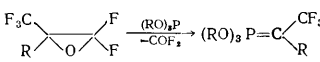
(LII, a–c)

R = Me (a), Et (b), iso-Pr (c);



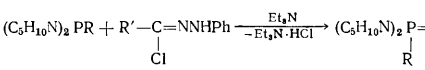
(LII) .

It has been shown recently that the epoxy-derivatives of perfluorinated alkenes give rise to ylides on interaction with trialkyl phosphites[77]:



$R = CF_3$, CO_2R'

The amides of tervalent phosphorus acids react with *C*-ethoxycarbonyl- and *C*-acetyl-*N*-arylnitrile imines to form stable azomethylenephosphonium ylides (LIII)[78]:



(LIII)

$R = C_5H_{10}N$, Ph; $R' = CO_2Et$, C (O) CH_3 .

3. The Synthesis of Ylides from Phosphonium Salts

The simplest method of synthesis of phosphorus ylides is the "salt method", which is widely used, particularly in the preparation of dialkylaminophosphonium ylides.

The phosphonium salts (LIV) are dehydrobrominated by sodium amide to form the ylides (LV) containing the unsubstituted methylene group; they are colourless, comparatively stable liquids which can be vacuum-distilled[79]. The benzylides (LVI) have been obtained by treating a phosphonium salt with butyl-lithium or sodium ethoxide[80,81]:

$$\underset{(LIV)}{(Me_2N)_n(Me)_{4-n}\overset{+}{P}Br^-} \xrightarrow[-NaBr]{NaNH_2/NH_3} \underset{(LV)}{(Me_2N)_n(Me)_{3-n}P{=}CH_2} \ ;$$

$$\underset{(LVI)}{(R_2N)_3\overset{+}{P}CH_2PhHal^-} \xrightarrow[(-HHal)]{BuLi;EtONa} (R_2N)_3P{=}CHPh \ ;$$

$R = Me$, Et; $n = 1 - 3$.

Stable ylides containing alkoxycarbonyl or diethylaminocarbonyl groups at the ylide carbon atom and primary or secondary amino-groups at the phosphorus atom have been obtained by treating the corresponding phosphonium salt with an aqueous solution of alkali, sodium ethoxide, or potassium t-butoxide[80–82].

The dehalogenation of trihalogenomethylphosphonium salts by triphenylphosphine or phosphorous acid tris(*N*,*N*-dimethylamide) constitutes a preparative method for the synthesis of dialkylaminophosphonium ylides containing a dihalogenomethylene group[83–85]:

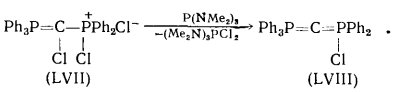
$$(Me_2N)_3\overset{+}{P}CHaI_3Hal^- \xrightarrow[-R_3PHal_2]{R_3P} [(Me_2N)_3P{=}CHal_2] \xrightarrow{R'_2C=O} R'_2C{=}CHal_2 \ ;$$

$R = Me_2N$, Ph; Hal = Cl, Br, F .

Ylides are usually obtained, without the isolation of the phosphonium salts, by treating the phosphorous acid tris(*N*,*N*-dimethylamide) with carbon tetrahalide. This results in the formation of extremely reactive ylides, which are readily converted into ketones and olefins[86–88]:

$$2(Me_2N)_3P + BrCCl_3 \xrightarrow[-20^\circ \div -10^\circ]{} [(Me_2N)_3P{=}CCl_2] + (Me_2N)_3PClBr \quad .$$

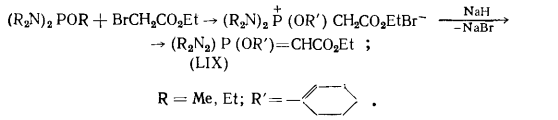
Carbodiphosphorane (LVIII) has been obtained by treating the ylide (LVII) with phosphorous acid triamide[89]:



(LVII) (LVIII)

The "salt method" is hardly used for the synthesis of ylides with alkoxy-groups at the phosphorus atom in view of the instability of the alkoxyphosphonium salts.

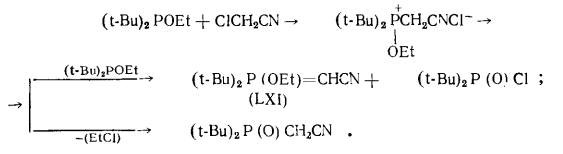
A rare example of this kind has been described recently[90]. The formation of the ylides (LIX) proved to be possible as a result of the unique stability of vinyloxyphosphonium salts:



(LIX)

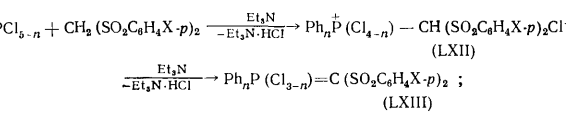
R = Me, Et; R′ = .

The ylide (LXI) with the ethoxy-group at the phosphorus atom was detected among other products after the reaction of ethyl di-t-butylphosphinite with chloroacetonitrile. It has been suggested that the intermediate phosphonium compound (LX) is dehydrochlorinated by the phosphinite in the reaction. The Arbuzov dealkylation of the phosphonium salt (LX) takes place simultaneously[91]:



(LXI)

Polychlorophosphoranes react readily with bis(arenesulphonyl)methanes in the presence of triethylamine. The phosphonium salt (LXII) formed initially is dehydrochlorinated by triethylamine and is converted into the *P*-chloroylide (LXIII) with a high yield[92]. The reaction is preparatively very simple and makes it possible to obtain ylides with both one and two chlorine atoms at the phosphorus atom:

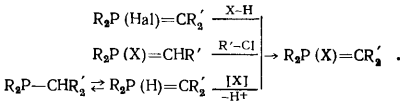


(LXII) (LXIII)

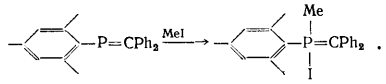
$n = 1,2$; X = H, Cl, Me, OMe .

4. The Conversion of Phosphorus Ylides of one Type into Phosphorus Ylides of Another Type

The conversion of ylides of one type into those of another provides extensive possibilities for the synthesis of *P*-hetero-substituted ylides. Thus *P*-halogeno-ylides readily exchange their mobile halogen atom for different groups in their reactions with nucleophiles, which makes it possible to introduce virtually any substituents at the phosphorus atom[14]. The hydrogen atoms at the ylide carbon atom are also readily substituted by other groups on interaction with chlorine-containing electrophiles[28,79]. The oxidative ylidation of tervalent phosphorus CH acids can be regarded to some extent as conversion of ylides of one kind into those of another. The CH acids are regarded as tautomeric forms of PH ylides[26,27]:



The synthesis of *P*-hetero-substituted ylides of one type into those of another type is discussed below in the section devoted to the properties of these compounds. The synthesis of *P*-hetero-substituted ylides from tervalent phosphorus compounds with a P=C bond is extremely interesting, although this method has been hardly developed further. A single example of the conversion of the acyclic phosphene (LXIV) into the ylide (LXV) with an iodine atom at the phosphorus atom is known[93]:



(LXIV) (LXV)

III. PROPERTIES

The properties of *P*-hetero-substituted phosphorus ylides are quite varied. The heteroatoms at the phosphorus atom of the P=C group alter the positive charge on the phosphonium cation and influence the nucleophilic properties of the ylides. In many instances, as a consequence of their mobility, the heteroatoms alter significantly the behaviour of ylides in chemical reactions. *P*-Hetero-substituted ylides therefore acquire properties which are lacking in triphenylphosphonium ylides. *P*-Hetero-substituted ylides are very reactive, are involved in many interesting reactions, and are valuable starting materials for the synthesis of many organic compounds.

1. Physical and Physicochemical Properties

In a pure state, the *P*-hetero-substituted phosphorus ylides are liquid or crystalline substances. Their stabilities differ greatly. Ylides having electron-accepting groups at the α-carbon atom capable of delocalising the negative charge of the carbanion are particularly stable. For example, the ylides (LXIII) with arenesulphonyl groups can be stored indefinitely and withstand heating to 200 °C.[14,21] However, unstable ylides, which exist only in solutions, are encountered. The "unstabilised" ylides, containing an unsubstituted methylene or alkylidene group, are oxidised very readily and hydrolysed in air[28,79,81].

P-Hetero-substituted phosphorus ylides have been investigated by various spectroscopic methods. The P=C group vibration frequencies have been observed in the infrared spectra of *P*-hetero-substituted ylides in the range 1000–1080 cm^{-1}.[18,28] A characteristic feature of ylides stabilised by carbonyl groups is the bathochromic shift of the absorption bands of these groups as a consequence of the conjugation with the negative charge of the ylide carbon atom[14,15,28,94,95]. The $\nu_s(SO_2)$ and $\nu_{as}(SO_2)$ absorption bands also undergo a bathochromic shift of approximately 70–80 cm^{-1} under the influence of the negative charge of the ylide carbon atom[14,21].

The ^{13}C and ^{31}P NMR spectra of *P*-hetero-substituted phosphorus ylides agree with their dipolar structure. The chemical shifts of the ^{31}P signals (Table 1) are located in a

weak field in direct proximity to the values of δp characterising the phosphonium cation $R_3\overset{+}{P}$ in phosphonium salts[28, 95,96]. On the other hand, the chemical shifts of the ^{13}C signals (relative to tetramethylsilane) are observed in a strong field in the region characteristic of the corresponding carbanions.

Table 1. The chemical shifts of the ^{31}P signals in the NMR spectra of *P*-hetero-substituted phosphorus ylides $RR'P(X)=CR''_2$.

X	R	R′	δp, p.p.m.	Refs.
H	Alk	Alk	20—40	[18, 25]
OH	Ph	Ph	47—50	[97, 98]
AlkO	AlkO	AlkO	50—57	[14, 65]
AlkO	Alk	Alk	82—92	[14, 37, 91]
AlkO	Ph	Ph	50—55	[65, 97, 98]
AlkNH	AlkO	AlkO	50—55	[14, 99]
AlkNH	AlkO	AlkO	40—45	[14, 99]
Alk_2N	AlkO	AlkO	55—60	[14]
Alk_2N	Alk	Alk	60	[22]
Alk_2N	Alk_2N	Alk_2N	59—65	[70, 100]
Me_3Si	iso-Pr	iso-Pr	37	[25, 46]
Alk_2P	Alk	Alk	14—30	[37, 46, 49]
Alk_2P	Ph	Ph	40	[49—51]
Cl	Me	Me	60	[37]
Cl	Alk	Alk	90—117	[27, 28, 101]
Cl	Alk_2N	Alk	95—105	[28]
Cl	Alk_2N	Alk_2N	60—70	[30, 38]
Cl	Ph	Ph	55—60	[38, 97, 98]
Br	t-Bu	t-Bu	100—126	[25, 26, 28]

Table 2. The tautomeric composition of dialkylbis(methoxycarbonyl)methylphosphines (in chloroform at 20 °C)[18,96].

R	R′	A, %	B, %
t-Bu	iso-Pr	39	61
t-Bu	s-Bu	35	65
t-Bu	Me_3SiCH_2	10	90
t-Bu	iso-Bu	67	33
t-Bu	n-Bu	65	35
n-Bu	n-Bu	85	15
iso-Bu	iso-Pr	70	30
t-Bu	Me_2N	100	0
t-Bu	Et_2N	100	0

2. Ylides with a P—H Bond

Alkylphosphines containing an α-hydrogen atom can be regarded as carbon analogues of tervalent phosphorus OH acids. Almost all the known OH acids of this kind exist in the tetracoordinate prototropic P(O)H form[102], which can be explained by the high energy of formation of the P=O bond ($E_{P=O}$ = 140 kcal mol^{-1}). On the other hand, the majority of alkylphosphines exist in the tricoordinate CH form owing to the inadequate thermodynamic stability of the PH ylide form. The ylide form can be stabilised by introducing two alkoxycarbonyl groups at the α-carbon atom as a consequence of the effective delocalisation of the negative charge of the ylide carbon atom over the conjugated bond system[18,25].

Thus dialkylbis(methoxycarbonyl)methylphosphines isomerise completely or partly to ylides with a P—H bond (Table 2):

$$\underset{(A)}{RR'P{-}CH(CO_2Me)_2} \rightleftarrows \underset{(B)}{RR'P(H){=}C(CO_2Me)_2}\ .$$

Dialkylbis(methoxycarbonyl)methylphosphines are stable substances which can be vacuum-distilled without decomposition and can be stored satisfactorily at the usual temperature. Some of them [compounds (LXVI)—(LXVIII)] have been obtained in the pure crystalline PH ylide form (B)[18,25]:

$$\begin{array}{c} t\text{-Bu}(R)P{=}C(CO_2Me)_2 \\ | \\ H \end{array}$$

R= iso-Pr (LXVI), t-Bu (LXVII), Me_3SiCH_2 (LXVIII)

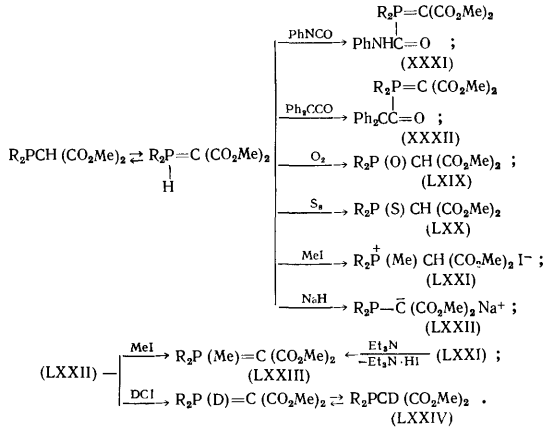
Dialkylbis(methoxycarbonyl)methylphosphines exist in solution as tautomeric mixtures of the prototropic forms (A) and (B), which has been demonstrated by spectroscopic studies. The signals of the protons of the CH and PH groups have been detected in the ^1H NMR spectra of these compounds. The signal of the proton of the PH group is split owing to the interaction with the phosphorus atom ($^1J_{PH}$ = 440 Hz). The signals of the CH form (singlet) and the PH form (doublet) with a coupling constant of 440 Hz are present in the ^{31}P NMR spectra. When the spin—spin coupling of the phosphorus nuclei with the protons is suppressed, the doublet is converted into a singlet, which confirms unambiguously the presence of a bond between the phosphorus atom and the hydrogen atom.

The tautomeric equilibrium (A) ⇌ (B) depends on the temperature and on the nature of the solvents and substituents at the phosphorus atom. The study of the thermodynamics of the tautomeric equilibrium led to the conclusion that the ylide form has a higher formation energy than the phosphine form [$\Delta H = -2.4 \pm 0.2$ kcal mol^{-1}, $\Delta S = -7.4 \pm 0.7$ e.u. for compound (LXVI) in chloroform][18].

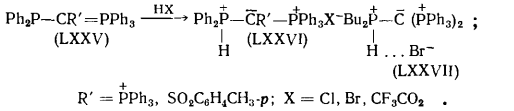
The results presented in Table 2 show that bulky and branched alkyl substituents stabilise the PH ylide form and displace the tautomeric equilibrium towards it. Examination of the Stuart—Briegleb models has led to the conclusion that bulky alkyl substituents are more favourable for the tetracoordinate PH ylide form, since the latter is sterically less hindered than the tricoordinate CH form[18,25]. It is quite evident that the influence of branched alkyl substituents on the position of the tautomeric equilibrium is associated with steric and not polar effects. According to modern ideas, alkyl groups (Me, Et, iso-Pr, t-Bu, etc.) are electrically neutral and differ only by their steric characteristics[103].

The chemical properties of ylides with a P—H bond are similar to those of other tervalent phosphorus CH acids as a consequence of the involvement of the tricoordinate form (A) in the tautomeric equilibrium[18,25,96]. They are oxidised, combine with sulphur, and are alkylated by alkyl halides with formation of phosphine oxides (LXIX), phosphine sulphides (LXX), and phosphonium salts (LXXI). At the same time dialkylbis(methoxycarbonyl)methylphosphines readily enter into oxidative ylidation reactions. The interaction with phenyl isocyanate and diphenylketen yields the *P*-substituted ylides (XXXI) and (XXXII). On interaction with sodium hydride, PH ylides are converted into the α-phosphinocarbanions (LXXII). The reaction of α-phosphinocarbanions with methyl iodide takes place at the phosphorus atom with formation of the ylide (LXXIII) (the "ylide variant" of the Michaelis—Becker reaction), while their reaction with deuterium chloride results in the formation of deuterated dialkylbis(methoxycarbonyl)methylphosphines (LXXIV), which consist of a tautomeric mixture of the CD and PD forms[18,25,96] (Scheme 8).

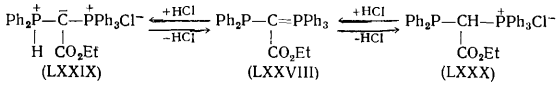
Scheme 8



The phosphinophosphonium ylides (LXXV), containing electron-accepting substituents at the α-carbon atom, are protonated by strong acids at the phosphorus atom[104-107]. X-Ray diffraction analysis of compound (LXXVII) not only confirmed the presence of the P–H bond but also showed that the proton retains to some extent its bond with the halogen[108-110]:



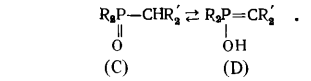
Detailed studies of the protonation of phosphinophosphonium ylides established that compound (LXXVIII) reacts with an excess of hydrogen chloride in methylene chloride at −80 °C with formation of the PH and CH forms of compounds (LXXIX) and (LXXX), between which equilibrium is established[109-112]:



These forms are unstable and exist only in solution at a low temperature, decomposing fully with cleavage of the P–C bond at −20 °C. The position of the tautomeric equilibrium (LXXIX) ⇌ (LXXX) depends on the temperature and the polarity of the solvent. The ratio of the CH and PH forms also depends on the concentration of hydrogen chloride, whence it follows that the interconversion of the forms occurs as a result of the reversible addition of HCl to and its elimination from the phosphinophosphonium ylide (LXXVIII). The involvement of hydrogen chloride in the prototropic equilibrium constitutes a significant difference between the tautomerism of the protonated phosphinophosphonium ylides and the phosphine–PH ylide tautomerism of dialkylbis(methoxycarbonyl)methylphosphines. The nature of the anion is also very important in this instance. For example, when hydrogen chloride is replaced by trifluoroacetic acid, protonation takes place only at the phosphorus atom of the phosphinophosphonium ylide (LXXVIII), the PH form is produced, and the CH form disappears[110].

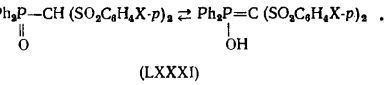
3. Ylides with a P–O Bond

Ylides with an OH group are tautomeric forms of alkylphosphine oxides:



The majority of alkylphosphine oxides exist in the CH form (C) as a consequence of the high basicity of the ylide carbon atom. The tautomeric equilibrium (C) ⇌ (D) is displaced towards the OH form (D) in the case of diphenylbis(arenesulphonyl)methylphosphine oxides (LXXXI), which contain substituents with strong electron-accepting properties[97,98,113].

In the crystalline state these phosphine oxides exist in the pure CH phosphine oxide form while in solutions they consist of a tautomeric mixture of the OH ylide and the CH phosphine oxide forms (Table 3)[97,98]:



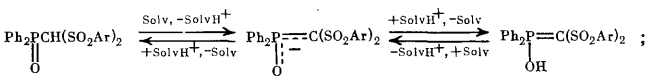
(LXXXI)

Table 3. The tautomeric composition of diphenylbis(benzenesulphonyl)methylphosphine oxides (LXXXI) (tetrahydrofuran at 25 °C)[96-98].

X	C, %	D, %
Cl	45	55
H	80	20
Me	90	10
MeO	96	4

The OH and CH forms can be readily detected by spectroscopic methods (infrared, ^{1}H, NMR, and ^{13}P NMR spectroscopy). The study of the process with the aid of dynamic NMR indicates a high rate of the interconversion of the tautomeric forms (the temperature at which the ^{31}P signals merge for the system in chlorobenzene is 100 °C for an external magnetic field strength of 81 MHz)[96]. The tautomeric equilibrium (C) ⇌ (D) is mobile and depends on the temperature and nature of the solvents and the substituents. The content of the ylide form increases with decrease of temperature and this form is evidently energetically more favourable. Electron-accepting substituents in the *para*-positions in the arenesulphonyl groups increase the content of the ylide form, because they enhance the delocalisation of the negative charge of the ylide carbon atom.

The study of the prototropic equilibrium in aqueous alcoholic solutions showed that a two-stage mechanism of the tautomeric transformation, with formation of the common anion (LXXXII), operates in these solvents, which have a high dissociating capacity:

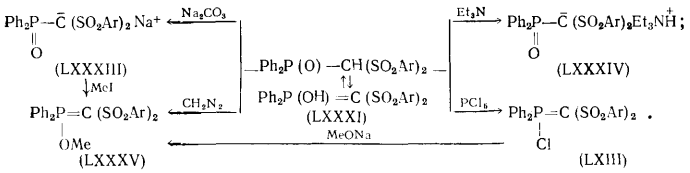


(LXXXII)

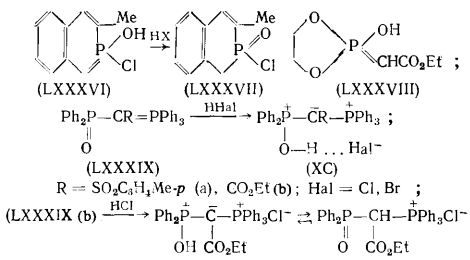
Solv = solvent.

Diphenylbis(arenesulphonyl)methylphosphine oxides have interesting properties, resembling those of the OH acids of tetracoordinate phosphorus. These extremely stable compounds are comparatively strong acids (pK_a = 3.55–3.68 in 50% alcohol). They readily dissolve in an aqueous solution of sodium carbonate, from which they can be recovered quantitatively on acidifying the solution; they react with triethylamine to form the stable triethylammonium salts (LXXXIV). The reaction of phosphine oxide with diazomethane leads to the formation of an *O*-methylated product—the ylide (LXXXV). The formation of the product (LXXXV) substituted at the oxygen atom is accompanied by the interaction of the sodium salt (LXXXIII) with methyl iodide. The reaction of compounds (LXXXI) with phosphorus pentachloride gives rise to the *P*-chloro-derivatives (LXIII) (Scheme 9).

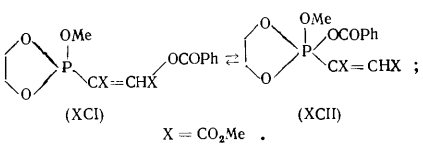
Scheme 9



The phosphine oxide–ylide tautomerism was first discovered and investigated in relation to diphenylbis(arenesulphonyl)-methylphosphine oxide[97,98,113]. Subsequently other OH ylides were also described. The cyclic *P*-hydroxy-λ^5-phosphorin (LXXXVI), which is stable in the crystalline state and which rearranges irreversibly to the more stable isomer (LXXXVII) with a P=O group in the presence of proton-donating reagents, has been synthesised[114]. It has been established[115] that the five-membered dioxaphospholan ring effectively stabilises the OH ylide form (LXXXVIII). The phosphine oxide phosphonium ylides (LXXXIX) are protonated by strong acids at the oxygen atom of the P=O group[106,116,117]. X-Ray diffraction analysis of compound (XCa) showed that the OH form is stabilised by a strong O–H...Br bond and that the H...Br distance is 2.24 Å, which is much less than the sum of the van der Waals radii (3.11 Å)[116]. The hydrochloride salt of the ylide (LXXXIXb) exists in the crystalline state in the OH form, while in solutions it is a mixture of the CH and OH forms in proportions of 1:1.8 (Mastryukova et al.[117]):



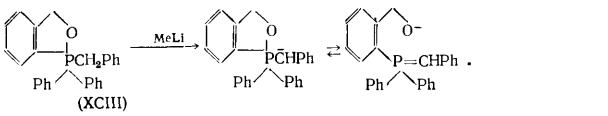
The tautomeric equilibrium between the ylide and phosphorane structures (XCI) ⇌ (XCII), which has been investigated by ^{31}P NMR,[71] is of considerable interest:



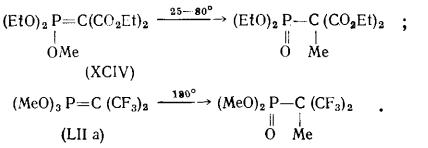
The position of the tautomeric equilibrium (XCI) ⇌ (XCII) depends on the nature of the solvent in the following way:

Solvent	(XCI)	(XCII)
CCl_4	18%	82%
CH_2Cl_2	37%	63%

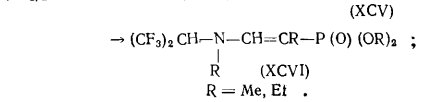
Another example of the ylide–phosphorane tautomeric equilibrium was found in the metallation of the phosphorane (XCIII) with a benzyl group[118]:



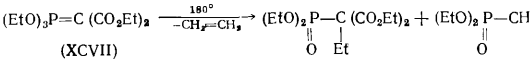
The ylides containing alkoxy-groups at the phosphorus atom are readily dealkylated and converted into phosphonates. Thus the alkoxyphosphonium ylides (LIIa) and (XCIV) rearrange on heating to phosphonates with migration of the alkyl group to the ylide carbon atom (the ylide version of the Pishchimuka reaction)[15,77]:



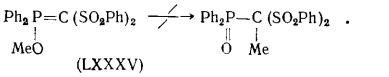
The ylides (XCV) are converted into the phosphonates (XCVI) already in their preparation reaction[119]:



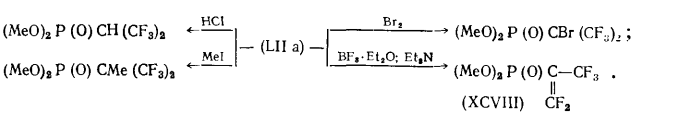
The ylides (XCVII) with ethoxy- or isopropoxy-groups at the phosphorus atom are more stable than the corresponding ylides (XCIV) with methoxy-groups. They are converted into phosphonates only on heating to 150–180 °C and the rearrangement is complicated by the elimination of an alkene[14]:



Electron-accepting substituents, which reduce the nucleophilicity of the ylide carbon atom, hinder the rearrangement. The ylide (LXXXV), containing the powerful electron-accepting benzenesulphonyl groups at the α-carbon atom, is stable and does not change on heating to 200 °C[14]:



Alkoxyphosphonium ylides are dealkylated on interaction with hydrogen chloride, bromine, and alkyl halides[14,16,76]. When the ylide (LIIa) was treated with boron trifluoride etherate, the "phosphorus analogue" of the perfluoromethacrylic ester (XCVIII) was obtained as a result of the simultaneous dealkylation and the elimination of a fluorine atom[120,121]:



Hydrolysis of ylides containing alkoxy-groups at the phosphorus atom proceeds both with elimination of one of the alkyl groups and with cleavage of the P=C bond[63,120].

Alkoxyphosphonium ylides normally undergo the Wittig reaction and their reactivities are probably comparable to those of triphenylphosphonium ylides. However, there are

very few data on this question[95]:

$$(\text{iso-PrO})_2(Et_2N)P{=}CHCO_2Et \xrightarrow{ArCHO} ArCH{=}CHCO_2Et + (\text{iso-PrO})(Et_2N)PO \ ;$$
$$Ar = Ph,\ p\text{-}O_2NC_6H_4 \ .$$

4. Ylides with a P–N Bond

Ylides with dialkylamino-groups at the phosphorus atom are available and are very reactive, which aroused much interest in these compounds by investigators. The reactivity and stability of dialkylaminophosphonium ylides depend on the substituents at the ylide carbon atom. Dialkylaminophosphonium ylides stabilised by electron-accepting substituents are indeed very stable. The azomethylenephosphonium ylide (LIII) hydrolyses only after prolonged refluxing in aqueous alcoholic solution. This involves the cleavage of the P–N and not the P=C bond and the amine formed converts the ethoxycarbonyl group into a carbamoyl group[78]:

$$(C_5H_{10}N)_3P{=}\underset{\underset{CO_2Et}{|}}{C}{-}N{=}NPh + H_2O \rightarrow (C_6H_{10}N)_2P(O){-}\underset{\underset{CO_2Et}{|}}{C}{=}NNHPh + C_5H_{10}NH \rightarrow$$
(LIII)
$$\rightarrow (C_5H_{10}N)_2P(O){-}\underset{\underset{C(O)NC_5H_{10}}{|}}{C}{=}N{-}NHPh + EtOH \ .$$

The ylide (XCIX) does not change even after heating at 140 °C for 4 h in 50% KOH, but it is reactive in the Wittig reaction[81]:

$$(Et_2N)_3P{=}CHCONEt_2 \xrightarrow{p\text{-}O_2NC_6H_4CHO} p\text{-}O_2NC_6H_4CH{=}CHCONEt_2 \ .$$

On the other hand, the unstabilised dialkylaminophosphonium ylides or the same ylides stabilised by weak electron-accepting substituents hydrolyse very readily and are oxidised by atmospheric oxygen. The ease of the reaction of the benzylide (LVIa) with atmospheric oxygen, in which it is converted into stilbene in a high yield, is so great that it actually interferes with its isolation in a pure form[81]:

$$[(Et_2N)_3P{=}CHPh] \text{ (LVI a)} \begin{cases} \xrightarrow{p\text{-}O_2NC_6H_4CHO} p\text{-}O_2NC_6H_4CH{=}CHPh \ ; \\ \xrightarrow{O_2} PhCH{=}CHPh + (Et_2N)_3PO \ . \end{cases}$$

The ylide (LV) having a methylene group reacts with chlorine-containing electrophiles, being converted in high yields into new types of dialkylaminophosphonium ylides (C) and (CI). The reaction is carried out with a reactant ratio of 2:1, since one ylide molecule is consumed in the dehydrochlorination of the intermediate phosphonium salt[79]:

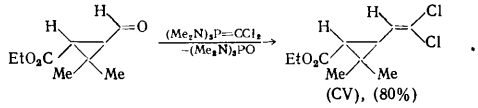
$$(Me_2N)_3P{=}CH_2 \begin{cases} \xrightarrow[-(Me_2N)_2(Me)\overset{+}{P}Cl^-]{PCl_3} [(Me_2N)_3P{=}CH]_3P \ ; \\ \xrightarrow[-(Me_2N)_2(Me)P^+Cl^-]{R_2PCl} (Me_2N)_3{=}CHPR_2 \ ; \end{cases}$$
(C) (CI)
$$R = Me, Et, OEt, NMe_2$$

Diazonium salts couple directly with dialkylaminophosphonium ylides. Phenyldiazonium fluoroborate reacts with the ylide (CII) to form the phosphonium salt (CIII), which can be converted into a new ylide (CIV) by treatment with sodium ethoxide[78]:

$$(C_5H_{10}N)_2P(Ph){=}CHCO_2Et \xrightarrow{PhN_2^+BF_4^-} (C_5H_{10}N)_2\overset{+}{P}(Ph)\underset{\underset{CO_2Et}{|}}{CH}{=}NPhBF_4^- \rightarrow$$
(CII) (CIII)
$$\xrightarrow{C_2H_5ONa} (C_5H_{10}N)_2P(Ph){=}\underset{\underset{CO_2Et}{|}}{C}{-}N{=}NPh \ .$$
(CIV)

As reactants in the Wittig reaction, dialkylaminophosphonium ylides are more reactive than triphenylphosphonium ylides. The electron-donating dialkylamino-groups weaken the electron-accepting properties of the phosphonium group, as a result of which the negative charge on the ylide carbon atom increases. Under the influence of strongly nucleophilic dialkylaminophosphonium ylides, even inactive ketones are converted into olefins and in the reactions with reactive carbonyl compounds there is a significant increase in the yields of olefins. The use of dialkylaminophosphonium ylides frequently yields satisfactory results in those cases where the triphenylphosphonium ylides are unsuitable. The compounds $(Me_2N)_3P{=}CF_2$[83] and $(Me_2N)_3P{=}CCl_2$,[86] generated *in situ* from $(Me_2N)_3P$ and carbon tetrahalides, are good sources of the trifluoromethylene and dichloromethylene groups for reactions with inactive ketones. The conversion of the ethyl ester of *cis,trans*-caronaldehydic acid into an olefin with the aid of $(Me_2N)_3P{=}CCl_2$ made it possible to obtain a high yield of a chrysanthemic acid derivative (CV)—an analogue of the natural insecticide permethrin (NRDC 143)[87] (Scheme 10).

Scheme 10

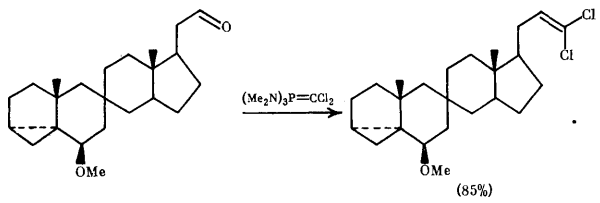


(CV), (80%)

Under analogous conditions, $Ph_3P{=}CCl_2$ gives a low yield of a highly contaminated compound (CV)[87].

It has been noted that the use of dimethylaminophosphonium ylides increases the stereospecificity of the Wittig reaction. It is significant, especially in studies with natural products, that, on treatment with these ylides, the optically active centres in the molecule are not involved and the compounds are not racemised[12,83] (Scheme 11).

Scheme 11



(85%)

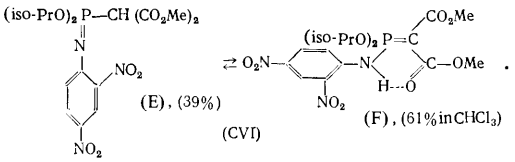
The ylides (F) containing NHR groups at the phosphorus atom are in a tautomeric equilibrium with the phosphazo-compound (E)[57,99]:

$$R_2P(O){-}CHR'CO_2R'' \rightleftarrows R_2P{=}CR'CO_2R''$$
$$\underset{\underset{NR'''}{\|}}{} \qquad \underset{\underset{NHR'''}{|}}{}$$
(E) (F)

The phosphazo-ylide tautomerism (E) ⇌ (F) obeys the rules of the acid–base prototropic equilibria and shifts towards the form which is a weaker acid under the given conditions. The introduction of more electron-accepting substituents at the nitrogen atom of the $-N-\underset{|}{P}-C\diagup\diagdown$ triad increases the content of the phosphazo-form (E) and, conversely, electron-accepting substituents at the carbon atom favour the formation of the ylide form (F)[57,99].

Depending on the substituents at the nitrogen and carbon atoms, the phosphazo–ylide equilibrium (E) ⇌ (F) can be displaced towards the preferential formation of one of the tautomeric forms or the forms (E) and (F) are present in comparable amounts (Scheme 12).

Scheme 12

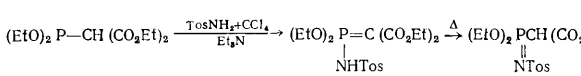


(E), (39%) (F), (61% in $CHCl_3$)

(CVI)

Thus compound (CVI) exists in the ylide form in the crystalline state, while in solutions it is present as a mixture of two tautomers. The ratio of the forms (E) and (F) depends on the temperature and the solvent. The study of the thermodynamics of the phosphazo–ylide tautomerism showed that the tautomeric equilibrium (E) ⇌ (F) is influenced by two opposed factors. On the one hand, the conversion of the phosphazo-form into the ylide form with its conjugation chain results in an energy gain $\Delta H = -6 \pm 0.6$ kcal mol^{-1}. On the other hand, this entails an increase of the rigidity of the molecule (since the ylide form is fixed by a strong intramolecular hydrogen bond) and the entropy diminishes ($\Delta S = -21 \pm 2$ e.u.). According to the equation $\Delta G = \Delta H - T\Delta S$, the equality of ΔH and $T\Delta S$ determines the equilibrium position. The presence of a strong intramolecular hydrogen bond has been confirmed by infrared and ^{1}H NMR spectra[57, 99, 124]. The migration of the proton between the nitrogen and carbon atoms in the $-N-\underset{|}{P}-C$ triad takes place readily and the interconversion of the tautomers (E) ⇌ (F) takes place comparatively rapidly.

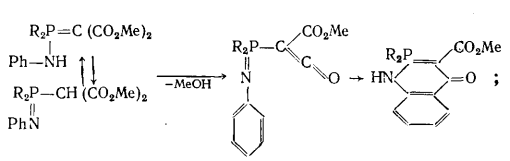
It has been reported[125] that the ylide with the tosylamide group at the phosphorus atom rearranges to the phosphazo-compound during the vacuum distillation of the reaction mixture formed in accordance with the equation



The conclusion that an ylide is formed and undergoes a rearrangement was reached on the basis of the presence in the infrared spectrum of the reaction mixture of an absorption band at 1650 cm^{-1}, which disappears on heating. The energy barrier to the prototropic rearrangement is unusually high, bearing in mind the high mobility of the NH proton of the tosylamide group, and apparently requires additional study and confirmation.

Anilinophosphonium bis(alkoxycarbonyl)methylides, which are stable under the usual conditions, evolve alcohol on heating to 150–180 °C and are converted into 2-phospha-4-quinolones (CVIII)[124]. The elimination of the alcohol results in the formation of the keten (CVII), whose cyclisation at the *ortho*-position of the benzene ring gives rise to 2-phospha-4-quinolone (Scheme 13).

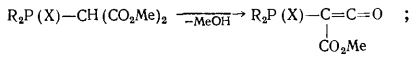
Scheme 13



(CVII) (CVIII)

R = EtO, iso-PrO, iso-Pr .

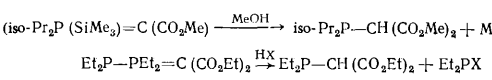
Under analogous conditions, the thermolysis of dialkylbis(methoxycarbonyl)methylphosphine oxides and phosphine sulphides leads to the formation of stable ketens[25]:



R = iso-Pr, t-Bu; X = O, S .

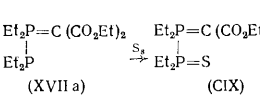
5. Ylides with P–Si, P–S, and P–P Bonds

The ylides containing the P–Si, P–S, and P–P bonds are stable liquids, capable of being vacuum-distilled, or crystalline substances. The P–P and P–Si ylides are readily cleaved at the phosphorus–element bond by various proton-donating reagents:



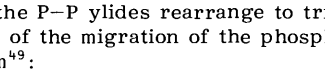
X = Cl, MeO, HO .

The P–P ylides are readily oxidised by atmospheric oxygen. The ylide (XVIIa) combines with sulphur via the tervalent phosphorus atom and is converted into the ylide (CIX) with the P(S)–P group; the P–P bond is then retained[14,48]:



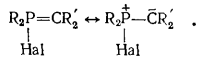
(XVII a) (CIX)

In certain cases, the P–P ylides rearrange to triphosphinomethanes as a result of the migration of the phosphino-group to the α-carbon atom[49]:



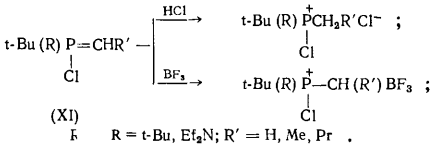
6. Ylides with Halogen Atoms at the Phosphorus Atom

P-Halogenoylides are promising reagents for organophosphorus synthesis. They are very reactive. The combination in one molecule of two active reaction centres (the nucleophilic centre consisting of the negatively charged carbon atom and the electrophilic centre consisting of the phosphonium carbanion to which the labile halogen atom is attached) is responsible for the wide variety and the specific features of the properties of these compounds:



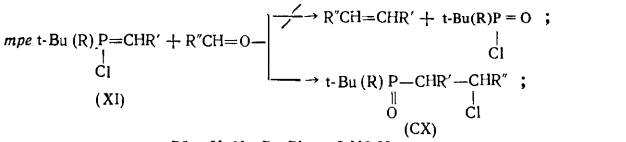
P-Halogenoylides react readily with both electrophiles and nucleophiles. Their reactivity in relation to electrophiles depends on the substituents at the carbanionic centre. The nucleophilicity and basicity of the *P*-halogenoylides containing powerful electron-accepting substituents R′ are low. Some of them (R′ = SO_2Ar) do not even give rise to stable phosphonium salts on interaction with hydrogen chloride. On the other hand, the "unstabilised" *P*-halogenoylides (XI, R′ = H or alkyl) are extremely reactive in relation to electrophiles. They combine with hydrogen chloride and boron trifluoride

via exothermic reactions and interact with carbonyl compounds, acid chlorides, etc.[27,28]:



(XI) R = t-Bu, Et_2N; R′ = H, Me, Pr .

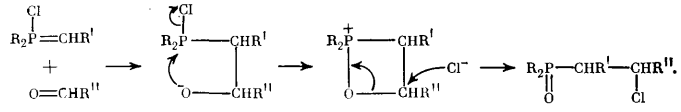
In contrast to triphenylphosphonium ylides, *P*-halogenoylides react with carbonyl compounds without the dissociation of the P=C bond, which results in the formation of organophosphorus products. *P*-Chloroylides do not form olefins on reaction with aldehydes, but give rise to β-chloroalkylphosphine oxides (CX)[101]. The reactions of *P*-chloroylides (XI) with aldehydes having different structures proceed at a low temperature and are accompanied by the evolution of heat. The yields of β-chloroalkylphosphine oxides (CX) are very high:



(XI) (CX)

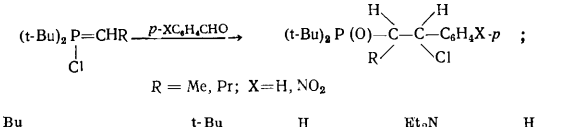
R″ = H, Me, Pr, Ph, *p*-$O_2NC_6H_4$.

The anomalous course of the reaction of *P*-chloroylides with aldehydes is due to the presence of the labile chlorine atom. As a consequence of the ability of the chlorine atom to ionise, an intermediate oxaphosphetanium salt (CXI) is formed. In contrast to the pentacoordinate intermediate compound in the Wittig reaction, this salt does not decompose into an olefin and a compound containing the P=O group, but is converted into a β-chloroalkylphosphine oxide as a result of the attack by Cl^- on the β-carbon atom via the mechanism of the Arbuzov rearrangement:

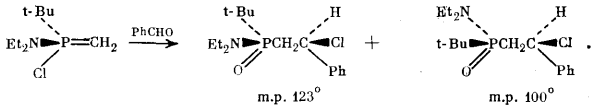


(CXI)

The reactions of *C*-alkyl-substituted *P*-chloroylides with aldehydes are stereoselective and lead to the formation of a single diastereoisomer of a β-chloroalkylphosphine oxide. However, the reactions of *P*-chloroylides having an asymmetrically substituted phosphorus atom are not distinguished by a high stereoselectivity and give rise to a mixture of diastereoisomers (in proportions of 1:2–2:3)[96,101]:

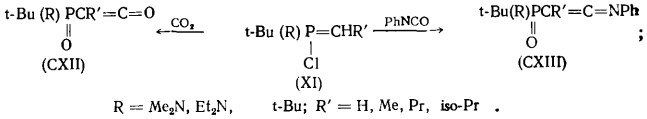


R = Me, Pr; X = H, NO_2



m.p. 123° m.p. 100°

The *P*-chloroylides (XI) react with carbon dioxide and phenyl isocyanate to form phosphorylated ketones and *C*-phosphorus-containing keten imines (CXII) and (CXIII)[27]:

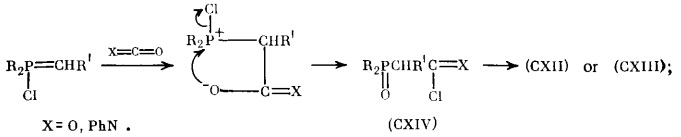


(CXII) (XI) (CXIII)

R = Me_2N, Et_2N, t-Bu; R′ = H, Me, Pr, iso-Pr .

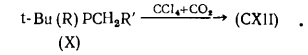
The reaction is carried out with an initial reactant ratio of 2:1, since one molecule of the ylide is consumed in the dehydrochlorination of the acid chloride (CXIV) formed at an intermediate stage (the reaction stops at the stage involving the formation of this acid chloride in the presence of a large excess of CO_2) (Scheme 14).

Scheme 14



X = O, PhN . (CXIV)

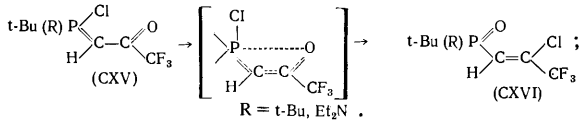
This method of synthesis of phosphorylated ketens and keten imines is preparatively fairly convenient. The initial *P*-chloroylides are formed from the tertiary phosphines (X) and CCl_4 and it is not obligatory to isolate them. The ketens (CXII) can be obtained directly from the tertiary phosphine (X) by treating it with CCl_4 and CO_2; the yields of the ketens are high:



(X)

The reactions of *P*-chloroylides containing a carbonyl group at the ylide carbon atom proceed via an analogous mechanism. The *P*-chloroylides (CXV), where there is a trifluoroacetyl group at the carbon atom, rearrange on heating to 120–150 °C to β-chlorovinylphosphine oxides (CXVI). The rearrangement takes place via a four-membered transition state, formed as a consequence of the intramolecular attack by the negatively charged oxygen of the C=O group on the positively charged phosphorus atom[126] (Scheme 15).

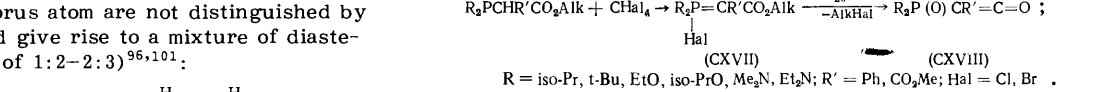
Scheme 15



(CXV) (CXVI)

R = t-Bu, Et_2N .

The *P*-halogenoylides (CXVII), containing an alkoxycarbonyl group, are converted into the phosphorylated ketens (CXVIII) even at room temperature and an alkyl halide is formed[25,127–129]:

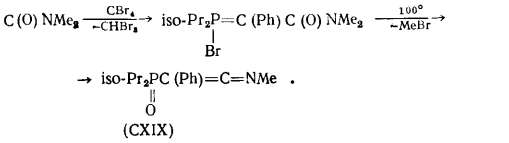


(CXVII) (CXVIII)

R = iso-Pr, t-Bu, EtO, iso-PrO, Me_2N, Et_2N; R′ = Ph, CO_2Me; Hal = Cl, Br .

The *P*-halogenylides (CXVII) are comparatively stable at 0 °C. They have been isolated in a pure state and characterised by the usual physical and chemical methods[14,25].

Diisopropyl-α-(*N*,*N*-dimethylcarbamoyl)benzylphosphine reacts with carbon tetrabromide to form a *C*-phosphorus-containing keten imine (CXIX) via the intermediate *P*-bromoylide[126]:



(CXIX)

The labile halogen atom attached to the $\overset{+}{P}$–C group in combination with the highly basic negatively charged ylide carbon atom determines the unusual "chlorinating" dehydrating

properties of *P*-chloroylides. Thus the reaction of the *P*-chloroylides (XI) with *N*-monosubstituted carboxylic acid amides results in the formation of imidoyl chlorides and phosphine oxides. The reactions take place in ether at a temperature below 0 °C and is accompanied by the evolution of heat[131]:

$$(XI) + PhC(O)NHR'' \rightarrow \begin{matrix} t\text{-Bu}(R)P(O)CH_2R' \\ + \\ PhC(Cl)=NR'' \end{matrix};$$

$R = t\text{-Bu}, Et_2N$; $R = H, Pr$; $R'' = Ph, p\text{-}ClC_6H_4$.

It has been suggested that the deprotonation of the amide by the ylide results in the formation of an ion pair containing the mesomeric anion $O-\overset{-}{C}-NR'$. The attack by the phosphonium cation on the oxygen atom of this anion gives rise to a quasi-phosphonium salt, which decomposes into an imidoyl chloride and a phosphine oxide[131] via Scheme 16.

Scheme 16

$$PhC(O)NHR' + R_2P(Cl)=CH_2 \rightarrow R_2\overset{+}{P}(Cl)-CH_2Me \; O=CPh(R'N) \rightarrow R_2\overset{+}{P}(Me)-O-C(Ph)=NR' \; Cl^- \rightarrow R_2P(O)Me + PhC(Cl)=NR' .$$

The primary amides of carboxylic acids are dehydrated by *P*-chloroylides (XI) and are converted into nitriles. Imidoyl chlorides are formed as intermediates and are dehydrochlorinated by the ylides to nitriles:

$$R''C(O)NH_2 \xrightarrow[-t\text{-}Bu(R)P(O)CH_2R']{(XI)} [R''CCl=NH] \xrightarrow[-t\text{-}Bu(R)(R'CH_2)PCl_2]{(XI)} R''C\equiv N .$$

The anilides of diphenylacetic and α-phosphorylated carboxylic acids react similarly with the *P*-chloroylides (XI) to form keten imines, while *N*,*N'*-disubstituted ureas are dehydrated by *P*-chloroylides to carbodiimides. The reaction of *P*-chloroylides (XI) with phosphaureas, providing a pathway to the synthesis of the heterocumulenes (CXX) with a dicoordinate phosphorus atom, are of special interest[96,131-133]:

$$R_2CHC(O)NHPh \xrightarrow{(XI)} R_2C=C=NPh ;$$

$R_2 = Ph_2$, t-Bu$_2$P(O)C(Me) ;

$$R-NHC(O)NH-Ph \xrightarrow{(XI)} R-N=C=N-Ph ;$$

$R = Ph$, t-Bu ;

$$RPHC(O)NHBu\text{-}t \xrightarrow{(XI)} RP=C=NBu\text{-}t .$$

(CXX)

P-Halogenoylides serve as the starting materials for the synthesis of a wide variety of organophosphorus compounds containing P=C bonds, including those which are difficult to obtain in other ways. Thus bis(methylene)phosphoranes (CXXII), the first compounds of quinquevalent tricoordinate phosphorus with two P=C bonds, have been obtained with the aid of the *P*-chloroylide (CXXI)[134]:

$$R-P(Cl)-C(SiMe_3)_2 \xrightarrow[-LiCl,-Cl_2C(SiMe_3)_2]{LiCCl(SiMe_3)_2} R-P[C(SiMe_3)_2]_2 ;$$

(CXXI) (CXXII)

$R = C_6H_{11}$, Ph, Me_2N .

In the reactions of *P*-chloroylides (XI) with chlorine-containing electrophiles (chlorotrimethylsilane, carboxylic acid chlorides, and tervalent phosphorus chlorides), the hydrogen atoms attached to the carbon atom of the P=C group are substituted and the new *P*-chloroylides (CXXIII)–(CXXVI), containing various substituents at the α-carbon atom, are formed[28] (Scheme 17).

Scheme 17

$$t\text{-Bu}(R)P(Cl)=CH_2 \rightarrow \begin{cases} \xrightarrow{R'C(O)Cl} mpe\ t\text{-Bu}(R)P(Cl)=CHC(=O)R' \ (CXXIII)\ (R'=CCl_3, CF_3) \\ \xrightarrow{Me_3SiCl} t\text{-Bu}(R)P(Cl)=CHSiMe_3 \ (CXXVI) \\ \xrightarrow{mpem\text{-}BuPCl_2} t\text{-Bu}(R)P(Cl)=CHP(Cl)Bu\text{-}t \ (CXXV) \\ \xrightarrow[(R=Et_2N)]{(Me_2N_2)PCl,CCl_4} t\text{-Bu}\,P(Cl)\,Cl\,P(NMe_2)_2\,CH\,NEt_2\;Cl^- \ (CXXVI) \end{cases} ;$$

$R = t\text{-Bu}$, Et_2N .

The halogen atom at the phosphorus atom in *P*-halogenoylides is exchanged for different substituents on interaction with nucleophiles containing a mobile hydrogen atom. The *P*-halides stabilised by electron-accepting groups are converted with high yields into all possible types of *P*-substituted ylides on interaction with alkylamines, aniline, ammonia, lithium phosphides, alcohols, phenols, thiols, and lithium alkyls[14,16,20,21,35,37,130]. These reactions are preparatively very simple and lead to extensive prospects for the synthesis of ylides containing virtually any substituents at the phosphorus atom in the P=C group (Scheme 18).

Scheme 18

$$R_2P(OAlk)=CR'_2 \xleftarrow{AlkOH+Et_3N\ (AlkONa)} R_2P(Hal)=CR'_2 \xrightarrow{NH_3} R_2P(NH_2)=CR'_2 ;$$

$$R_2P(OPh)=CR'_2 \xleftarrow{PhCNa} \qquad \xrightarrow{AlkNH_2} R_2P(NHAlk)=CR'_2 ;$$

$$R_2P(SAlk)=CR'_2 \xleftarrow{AlkSH+Et_3N} \qquad \xrightarrow{Alk_2NH} R_2P(NAlk_2)=CR'_2 ;$$

$$R_2P(R_2P)=CR'_2 \xleftarrow{R_2PLi} \qquad \xrightarrow{PhNH_2+Et_3N} R_2P(NHPh)=CR'_2 ;$$

$R = Alk, AlkO, Ph, Alk_2N$; $R' = CO_2R, SO_2Ph, SiMe_3, SiCl_3, Ph$; $Hal = Cl, Br$.

On the other hand, the unstabilised *P*-halogenoylides (XI) are converted with high yields into the phosphonium salts (CXXVII)–(CXXX) on interaction with compounds containing a mobile hydrogen atom (alcohols, phenols, ketoenols, alkylamines, hydrazoic acid, etc.)[130]. The CH acidity of the phosphonium salts is low and they are not dehydrochlorinated under the reaction conditions and are not converted into ylides. The reaction therefore stops at the stage involving the formation of addition products and not substitution products, as in the case of the stabilised *P*-halogenoylides:

Scheme 19

$$t\text{-Bu}(R)\overset{+}{P}(NHMe)MeCl^- \xleftarrow{MeNH_2} t\text{-Bu}(R)P(Cl)=CHR' \xrightarrow{AlkOH} t\text{-Bu}(R)\overset{+}{P}(OAlk)CH_2R'Cl^- \ (CXXVIII) ;$$

(CXXIX)

$$t\text{-Bu}(R)\overset{+}{P}(OAr)CH_2R'Cl^- \xleftarrow{ArOH} (XI) \xrightarrow{HN_3} t\text{-Bu}(R)\overset{+}{P}(N_3)MeCl^- \ (CXXX) ;$$

(CXXVII)

$$(XI) \xrightarrow{ArOH} t\text{-Bu}(R)\overset{+}{P}(Cl)CH_2R'OAr^- \rightarrow (CXXVII) .$$

(CXXXI)

The reactions of unstabilised *P*-chloroylides with compounds containing a mobile hydrogen atom take place in two stages. Initially the ylide carbon atom is protonated and the chlorophosphonium salt (CXXXI) is formed, after which the anion attacks the phosphonium cation to produce the phosphonium chloride (CXXVII). The chlorophosphonium salts (CXXXI) can be detected by spectroscopic methods[96,130].

It follows from the data examined here that the *P*-hetero-substituted phosphorus ylides can be used successfully in organic and organophosphorus synthesis. They successfully complement and significantly extend the applications of ylides as a whole. The introduction of various substituents not only at the carbon atom but also at the phosphorus atom of the P=C group makes it possible to control flexibly the properties of these reactive compounds.

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The Properties and Use in Catalysis of Zeolites of the Pentasil Type

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Progress in the study of the structure, physicochemical, and catalytic properties of high-silica zeolites of a new structural type—pentasils— has been reviewed. The bibliography contains 289 references.

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I. INTRODUCTION

In recent years in the field of zeolite catalysis, there has been intensive development of studies of the physicochemical and catalytic properties of zeolites of a new structural type—pentasils. These zeolites are characterised by an unusually high SiO_2 content, and are therefore sometimes called "super-high-silica" (SHS) zeolites. The best known of these materials are the Mobil Oil ZSM zeolites[1-6], for which x, the molar ratio SiO_2/Al_2O_3, usually lies in the range 12–100, but may reach much higher values. The final member of this series is silicalite[7], which does not contain any aluminium ($x = \infty$) and consists of crystalline silicon dioxide. Analogues of the ZSM zeolites have also been synthesised and are being extensively studied in the Soviet Union; in the Soviet scientific literature they are usually called SHS zeolites.

Interest in the new generation of zeolites increased after the publication, by Mobil Oil in 1974-75, of a large number of patents which showed that ZSM zeolites are much more effective catalysts for a number of processes of practical importance in petroleum refining and petroleum chemistry than their predecessors (faujasites, mordenite, etc.). Processes based on the use of ZSM zeolites include, for example, the catalytic dewaxing of petroleum fractions[8,9], the alkylation of aromatic hydrocarbons by alkenes[10], the aromatisation of individual C_2–C_4 alkenes and their mixtures[11-13], the cracking of gas oil fractions, giving a higher yield of aromatic hydrocarbons[16,17], the isomerisation of xylenes[18-21], and the conversion of synthetic gas into petrol[22]. In 1975, a number of patents[23-31] were published on the production of high-octane petrols (octane number ≥95) from various oxygen-containing and other heteroatomic compounds in the presence of ZSM zeolites.

A unique place among these processes is occupied by the production of high-octane petrol from methanol on ZSM zeolites[28,32-37]. This process, which at the time of the energy crisis and the search for new sources of energy revealed a realistic way of obtaining high-quality motor fuels without using petroleum raw materials, stimulated the study of the properties and potential use of the new zeolites as catalysts.

Although only slightly more than ten years have passed since the appearance of the first papers on pentasils, extensive information has accumulated in the literature on

the structure, physicochemical, and catalytic properties of these zeolites. These data have to some extent been reflected in a number of reviews of problems in zeolite catalysis[38-51]. Some of the reviews were published a comparatively long time ago, however, and they do not include recent results. The authors of other reviews either restricted themselves to an examination of data on the use of pentasils as catalysts of one single reaction, or use these data to illustrate the current state and trends in the development of zeolite catalysis. Thus in the compilation of the present review an attempt has been made, as completely as possible, to survey, systematise, and analyse data available in the scientific literature on zeolites of the pentasil family, with the exception of patents, although in a number of cases reference to these has been necessary.

II. SYNTHESIS, STRUCTURE, AND PHYSICOCHEMICAL PROPERTIES OF PENTASILS

The synthesis of zeolites is an independent and very specific field at the boundary between inorganic and physical chemistry. The main characteristics of the method of preparing pentasils will therefore be examined only briefly, and the conditions for their crystallisation and the regular features, kinetics, and mechanism of this process will not be discussed in detail. A large number of published papers have been devoted to these questions[52-61].

The synthesis of pentasils is based on the hydrothermal crystallisation of alkali aluminosilicate gels in the presence of the cations of organic bases. This method has been described in Mobil Oil patents dealing with the production of various representatives of the ZSM zeolite family[2-6]. At the present time this family alone includes more than fifteen different zeolites (ZSM-4, -5, -8, -10, -11, -12, -20, -21, -34, -35, -38, etc.), which are synthesised by varying the temperature of the process, the ratio of the components in the reaction mixture, and other conditions, and also using different organic compounds as additives.

The addition of organic bases (tetramethylammonium compounds) was first used in 1961 by Barrer[62,63] in the synthesis of the first generation of zeolites. The zeolites obtained in this way (zeolites of type A, erionite, chabasite, offretite, faujasite) were characterised by higher values of the ratio SiO_2/Al_2O_3 than the same zeolites synthesised in the absence of organic cations. In a development of this method, Mobil Oil studied the possible use in zeolite synthesis of tetraethyl-, tetrapropyl-, and tetrabutylammonium and tetrabutylphosphonium cations and the cations of pyrrolidine, ethylenediamine, and other organic compounds. This led to the preparation of the high-silica zeolites of the large ZSM family.

The study of these zeolites[5,6] showed that some of them, for example ZSM-21 and -34 zeolites, have a familiar structure (ferrierite and erionite–offretite respectively). At the same time, the zeolites ZSM-5, ZSM-11, and apparently ZSM-12 belong to a previously unknown pentasil structure[2-4] which has no natural analogues. The same structure is shown by silicalite and fluorosilicalite (analogues of ZSM-5), obtained in the presence of the tetrapropylammonium cation[64,65]; silicalite-2 (analogue of ZSM-11), synthesised using tetrabutylammonium cations[66]; and tetraethylammonium silicate (analogue of ZSM-12), which was crystallised in the presence of tetraethylammonium cations[67]. It is now known that zeolites with a pentasil structure can be synthesised using as organic additives, for example, lower aliphatic alcohols, or without using any organic additives[68].

In the ZSM zeolite family, the most detailed studies have been carried out for ZSM-5 and ZSM-11 zeolites[69-73], which show unusual catalytic properties, and also silicalite[48], the structural analogue of ZSM-5 zeolite. The ZSM-5 zeolite crystallises in the orthorhombic system with crystal lattice parameters $a \cong 20.1$, $b \cong 19.9$, and $c \cong 13.4$ Å, and the ZSM-11 zeolite crystallises in the tetragonal system with lattice parameters $a = b = 20.12$ Å and $c = 13.44$ Å. The composition of the unit cell of both zeolites in the Na form is given by the formula $Na_nAl_nSiO_{96-n}O_{192}\cdot\sim 16H_2O$, where $n < 27$ for ZSM-5 and $n < 16$ for ZSM-11. The densities of the crystal lattice of the zeolites ZSM-5 and ZSM-11 are 17.9 T and 17.6 T per 1000 Å^3 respectively (T = Si + Al).

The crystal lattice of ZSM-5 and ZSM-11 zeolites is based on structural elements (Fig. 1*a*) which consist of five-membered rings. Because of the low Al concentration (which can be determined with a high accuracy in the pentasil framework by X-ray diffraction[74]), these five-membered rings are formed chiefly by silicon–oxygen tetrahedra[69-72]. Chains of these elements (Fig. 1*b*) are connected in layers (Fig. 1*c*), and each chain in the layer is the mirror image of its neighbours. The layers of chains of structural elements can be connected in pairs in two ways. If the connection of two neighbouring layers is accompanied by their inversion relative to one another, a crystal lattice of the ZSM-5 zeolite type is formed, whereas with mirror arrangement of neighbouring layers, a crystal lattice of the ZSM-11 type is formed.

It has been suggested[70] that structurally, ZSM-5 and ZSM-11 zeolites are the extreme members of a very extensive series of mixed structures formed as a result of the large number of possible combinations of chains and layers of structural elements. All these structures belong to the pentasil family, which also includes silicalite, whose crystal lattice is made up of only silicon–oxygen tetrahedra[64].

The production of the crystal lattice of pentasils involves the formation of a system of channels which intersect one another at right angles and which in cross-section have the form of ten-membered rings (Fig. 1*c*). For ZSM-5 zeolite this system consists of straight and "sinusoidal" channels (Fig. 2*a*).[69,70,72] The straight channels in cross-section have the form of an almost regular circle (5.4 × 5.6 Å), and the cross-section of the sinusoidal channels has the form of an ellipse (5.1 × 5.5 Å). An analogous system of channels has been detected in silicalite, which differs from ZSM-5 zeolite only in the fact that the straight channels have an elliptical cross-section (5.0 × 5.6 Å), and the cross-section of the sinusoidal channels has the form of a circle with diameter 5.3 Å.[64] In contrast to ZSM-5 zeolite and silicalite, the system of pores in ZSM-11 is formed only by straight channels, which in cross-section have the form of an ellipse (5.4 × 5.6 Å) (Fig. 2*b*).[71,72] In a number of cases, the synthesis may be accompanied by the formation of zeolites of the pentasil family, having a mixed pore system (for example 2*c*).[47]

The unusual structures and composition of the pentasils give them characteristic catalytic and adsorption properties, which make them different from the first generation of zeolites. This raises the question of the reasons for the high catalytic activity of pentasils, which are characterised by a low aluminium content. According to existing ideas[1], the activity of zeolites in a whole series of catalytic reactions involving carbenium ions is due to the presence on their surface of acidic OH groups, joined to the Al atoms of the crystal lattice.

Of particular importance in this connection is the question, not yet fully resolved, of the localisation and distribution of Al atoms in the framework of pentasils. In the opinion of some authors[69-71], the small number of Al atoms is distributed

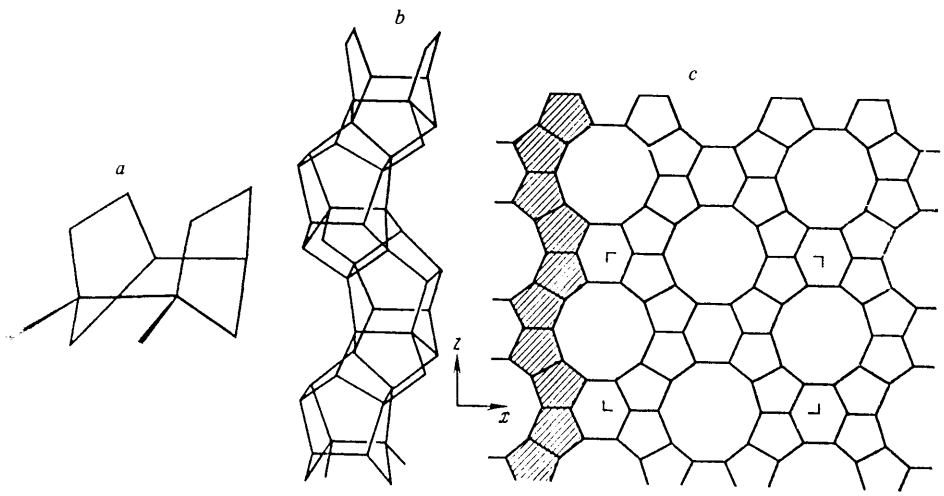


Figure 1. Schematic representation of the structural element (*a*), chains (*b*) of these elements, and the layer (*c*) formed by these chains, for ZSM-5 and ZSM-11 zeolites[69-72].

uniformly through the volume of the crystallites, as confirmed for ZSM-5 zeolites by Auger spectroscopy[75] and secondary ion mass spectrometry[76]. X-Ray photoelectron spectroscopy (XRPES), however, established[77] that the surface of specimens of the Na- and H-forms of ZSM-5 zeolite are enriched in silica. According to the data of other authors, obtained by the same method for ZSM-5 zeolite[78], and also for its analogues of the TsVK and TsVM type[79], the surface layers of the crystallites are enriched in alumina. This is also indicated by the results of a study of large (60–200 μm) crystallites of ZSM-5 zeolite by scanning electron microscopy and scanning X-ray microanalysis[53]. The conclusion that Al is uniformly distributed in pentasil crystallites was also reached in Refs.80–83.

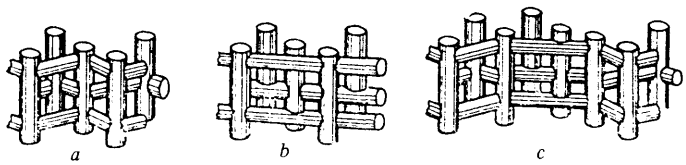


Figure 2. Schematic representation of the structure of the pores in zeolites of different types: *a*) ZSM-5 and silicalite, *b*) ZSM-11, *c*) mixed type[44,64,69-72].

The reasons for this are not completely clear. It is considered[53], for example, that enrichment of the surface layers of pentasil crystallites in aluminium is related to the characteristic features of the final stage of crystallisation. It is pointed out, however, that in small crystallites, the concentration of Al may be the same on the surface and in the volume. It is also known that the nature of the distribution of Al in pentasil crystallites may change with change in the conditions of thermal treatment and treatment with acids (see below).

Because of the low aluminium concentration, zeolites of the pentasil family have a much higher thermal stability than the zeolites of the first generation, whose structure in most cases breaks down at temperatures of 700–800 °C. In contrast to this, X-ray diffraction shows that heating ZSM-5 and TsVK zeolites at temperatures up to 1000° does not lead to breakdown of their crystal structure[2,78,84,85], and the structure of silicalite begins to become amorphous only at 1300°.[64] At the same time, according to XRPES,[78] high-temperature treatment apparently leads to the migration of ~15% of the Al atoms from the framework of the ZSM-5 zeolite. This may indicate slight breakdown of the zeolite structure at the points where aluminium is localised. The possibility of slight changes in the structure of pentasils on high-temperature treatment is also indicated by data on the change in the catalytic activity and selectivity of TsVK zeolite after its activation at 900–1000°.[84,85]

The ion-exchange properties of zeolites of the zeolite family are determined by the characteristic features of their composition. The presence of small quantities of aluminium in these zeolites determines the low value of the negative charge on their lattice and hence the low concentration of cations compensating these charges[57,86]. The latter include both Na^+ cations and the bulky non-exchangeable cations of organic bases (R_4N^+), used in the synthesis of the zeolite. The Na^+ cations, whose concentration in the original Na-form of the pentasils usually does not exceed 1.0–1.5% (calculated as Na_2O), can readily be replaced by NH_4^+ cations or protons by ion exchange with NH_4Cl or HCl. The organic cations are readily decomposed by heating the zeolite in air (350 to 450°), and are removed as ammonia, amines, and the corresponding hydrocarbons. The decationated or proton H-forms of the zeolites produced by this treatment have a higher sorptive capacity[2,86,87] and a higher catalytic activity[86-88] than the original Na form.

When caesium cations are introduced into the H-forms of a series of ZSM-5 zeolites with different compositions ($SiO_2/.Al_2O_3$ = 89–8660), a very good correlation is observed between the concentration of exchangeable caesium and the concentration of Al in the zeolite framework (Fig.3).[89] Thus the ability of pentasils to undergo ion exchange shows the

same dependence on the Al concentration in the crystal lattice as in the case of zeolites of the first generation. Moreover, the protons of the H-forms of ZSM-5, TsVK, and TsVM pentasils can be replaced by the cations of Na, Ca, Ag, the lanthanides, Pt, and Pd,[2,90,91] and this opens up new possibilities for the directed control of the catalytic properties of these zeolites.

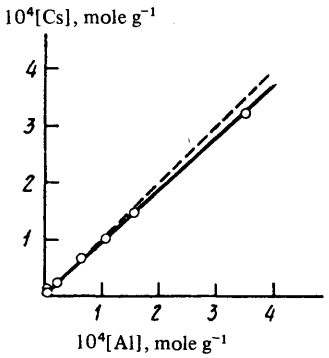


Figure 3. Influence of the Al concentration in the framework of H-ZSM-5 zeolite on its ability to undergo exchange with caesium[89]; the broken line corresponds to a ratio [Cs]/[Al] = 1.

Pentasils are much more hydrophobic than first-generation zeolites[2,64,89,92-95]. For ZSM-5 zeolite heated in air at 550°, the ratio of the quantities of sorbed n-hexane and water is ~1.5, whereas for zeolites of types A, X, and Y, the ratio is ~0.5.[2] According to other data[93], the same ratio (which for zeolites of types A, X, and Y, and mordenite is 0.4–0.9) increases to 1.4–2.4 for ZSM-5 and ZSM-11 zeolites. The water adsorbed by ZSM-5 zeolite occupies only 20–25% of the total volume of its pores[64,89]. For different ZSM-5 zeolite specimens in which the ratio SiO_2/Al_2O_3 varied from 75 to 8660 [89] and from 50 to 900,[95] with decrease in the Al concentration of the zeolite, the quantity of water sorbed by it decreased linearly to a very low value, corresponding to the adsorption of water by silicalite (~15 H_2O molecules per unit cell[64]). A similar result was obtained[96] for a number of ZSM zeolite specimens and their analogues with different Al concentrations.

These data on the hydrophobic properties of pentasils are in good agreement with the suggestion that there is a relationship between the affinity of the zeolites for water and the concentration of aluminium in them, and also that a bond is formed between the molecules of sorbed water and the protons joined to $[AlO_2]^-$ groups in the zeolite structure[94].

The hydrophobic character of the zeolites is combined with an ability to adsorb small molecules of various inorganic compounds. O_2, N_2, CO_2, and H_2S molecules easily penetrate into the channels of ZSM-5 and ZSM-11 zeolites[72], and the sorptive capacity of the latter is slightly lower, because of the characteristic features of its porous structure (see above). A significant contribution to the sorptive capacity of pentasils is apparently made by the cavities which are formed at the points of intersection of the channels and which have different shapes in ZSM-5 and ZSM-11. The H-form of ultrasil (an analogue of ZSM-8 zeolite) has a high sorptive capacity for hydrogen, equal to ~80% of its capacity for nitrogen[97].

A study of the adsorption of substances of different chemical character (inorganic compounds, hydrocarbons, methanol) on a zeolite of the ultrasil type[98,99] showed a definite relationship between the quantity of the substance sorbed by the zeolite and the volume of the sorbate molecules (Fig. 4). The curve giving this relationship shows a maximum in the region of n-heptane, whose existence was attributed to steric hindrance, preventing the diffusion into the pores of the zeolite of molecules with a chain length of more than seven carbon atoms. In contrast to this, for NaX zeolite, the quantity of adsorbed substance is independent of the volume of the adsorbate molecule.

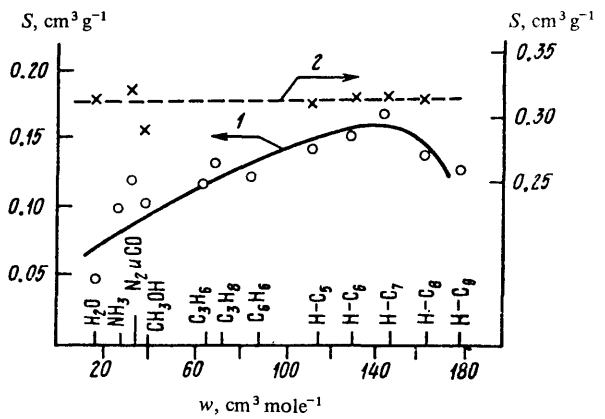


Figure 4. Change in the volume (S) of substances adsorbed by ultrasil (*1*) and NaX zeolite (*2*) on the volume of their molecules (w) (from published data[99]).

Pentasils readily adsorb normal alkanes[2-4,64,70,72,87,95,98-103]. The adsorption of branched alkanes and alkylaromatic and other hydrocarbons is limited considerably by the size and shape of the pores in the pentasils. For example, ZSM-5 zeolites readily adsorb n-hexane (4.3 Å)†, but sorb the isomeric methylpentanes (5.5 Å) and dimethylbutanes (6.1–6.3 Å) to a much smaller extent, and the extent of the sorption of these hydrocarbons decreases with increase in the degree of branching of the adsorbate molecules. H-ZSM-5 zeolite selectively adsorbs 2-methylpentane from its mixture (1:1) with 2,2-dimethylbutane[104,105]. Benzene, toluene, and *p*-xylene (which all have a diameter of 5.8 Å) are the aromatic hydrocarbons most readily adsorbed. An interesting feature is that the volume of benzene sorbed by H-ZSM-5 zeolite is much smaller than the volume of *p*-xylene. This is apparently because of the closer packing of the *p*-xylene molecules in the pores, and the interaction of the hydrogen atoms of this isomer with the surface of the walls of the zeolite pores[70,72].

The pore volumes occupied by adsorbed hydrocarbons with different structures are different, and always less than the true volume of the entire system of channels in the pentasil[72]. The system of pores in these zeolites is evidently not equally accessible to adsorbate molecules with different structures.

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†The figures in brackets give the values of the kinetic diameter of the molecules from Refs. 1 and 70.

The accessibility of the porous structure of pentasils (ZSM-5, ultrasil) to molecules of different hydrocarbons has been studied in detail[100,101,106]. The sorptive capacity of ZSM-5 zeolite for n-hexane is greater by approximately 30% and 50% than its capacity for 3-methylpentane and benzene respectively[72]. The sorptive capacity of pentasils depends to a significant extent on the nature of the adsorbate[107].

In the examination of sorption processes in zeolites, it is desirable to take account of the rate of penetration of the molecules into the pores of the adsorbent[108]. There are as yet, however, very few published data on the kinetics of sorption and diffusion for pentasils. The diffusion coefficients of benzene and *p*-xylene in ZSM-5 zeolite are approximately 10^3 times that for *o*-xylene, and 10^5 times those for 1,3,5-trimethylbenzene and pentamethylbenzene[70,109]. The initial rates of the adsorption of the xylene isomers in TsVK zeolite decrease in the following order[84]: *p*-xylene > *m*-xylene > *o*-xylene.

Thus pentasils whose maximum pore diameter is ~5.8 Å show clearly defined molecular-sieve properties. Unlike the first-generation zeolites, they can sorb molecules whose kinetic diameter exceeds the width of their channels by ~1 Å.[100] At the same time, in the pentasil pore system there is steric hindrance to the diffusion of molecules whose shape does not correspond to the shape of the zeolite channels[110,111].

Molecular-sieve properties of this kind, requiring correspondence between the size and shape of the adsorbate molecules and the pores of the adsorbent, were previously observed for various first-generation zeolites (zeolite of type A, erionite, mordenite, etc.).[110-112] As with these zeolites, the molecular-sieve properties of the pentasils have a significant influence on their catalytic properties. This influence is revealed as the so-called "configurational selectivity" (shape selectivity)[110] of catalytic reactions with respect to the original reagents, the products, or the transition state. These effects have made it possible to use pentasils as catalysts for dewaxing petroleum fractions[8,9], for the selective production of *p*-xylene[18-21,109], and for other processes[113].

The sorptive properties of pentasils depend both on the diameter and on the shape of the channels forming their porous structure. The straight and sinusoidal pores of ZSM-5 zeolite differ in relation to the adsorption and diffusion of hydrocarbons[70,72,102]. ZSM-5 zeolite has a higher sorptive capacity for hydrocarbons than ZSM-11 zeolite[114]. The geometry of the pores of ZSM-5 zeolite evidently corresponds more effectively to the shape of the molecules of the hydrocarbons being sorbed. A relationship has been established between the length of adsorbate molecules, the length of the channels in the pentasils, and their sorptive capacity, and it has been shown that the cavities which are formed by the intersection of the channels and which have different shapes in ZSM-5 and ZSM-11 zeolites play a part in the processes of sorption and diffusion[72,102]. In ZSM-11 zeolite, in which all the pores are straight, the molecules of normal and branched C_3–C_{10} hydrocarbons can be adsorbed in channels passing through the crystallite in only one crystallographic direction. In contrast to this, in ZSM-5 zeolite, small n-alkane molecules (C_3–C_5) are adsorbed in all the pores. Higher n-alkanes (C_6–C_8), C_4 and C_5 isoalkanes, and *p*-xylene are adsorbed only in the straight channels, and C_9 and C_{10} n-alkanes only in the sinusoidal channels. For the isomers of decane (methylnonanes), depending on the position of the methyl group in the chain, the adsorption of the isomers may take place only in the straight channels (4-methylnonane) or only in the sinusoidal channels (5-methylnonane) of ZSM-5 zeolite[72].

Published data on the adsorption of hydrocarbons on ZSM-5 zeolites[102] indicate that the movement of the molecules inside the crystallites is controlled by the pentasil pore system itself (molecular traffic control). According to this hypothesis, which has been questioned[115,116], in catalytic processes (for example the transformation of methanol into hydrocarbons), reagent molecules with a definite size diffuse into the crystallites along channels of one type, and the molecules of products with a different size are removed from the zeolite through channels of the other type. This should stop back-diffusion, which lowers the reaction rate.

The influence of the pore structure of pentasils on their molecular-sieve and catalytic properties is also revealed in the high stability of zeolites of this type with respect to coke formation, compared with first-generation zeolites. The restricted diameter of the channels in the pentasils, and the absence of large cavities, apparently prevent the formation, in the crystallites, of large molecules of polycondensed aromatic compounds, which cannot diffuse out of the pores and which provide one source of the coke which deactivates the catalyst[78,112,117-120]. In H-ZSM-5 zeolite, in contrast to mordenite and offretite, coke is formed on the outer surface of the crystallites, and not inside the pores, where the most strongly acidic centres, responsible for the catalytic activity of the pentasils, are situated[119]. In the transformation of C_3 and C_4 alkanes (450–550 °C), TsVK pentasils shows practically no loss of activity for 6–8 h, whereas zeolites of types A, X, and Y, and mordenite under the same conditions are rapidly deactivated as a result of intensive coke formation[121].

The shape and diameter of the pentasil channels evidently are not the only factors determining their adsorption and catalytic properties. For example, the study of the sorption of a series of hydrocarbons, methanol, and dimethyl ether on different specimens of H-ZSM-5 zeolite has shown[107,108] that the extent and kinetics of the sorption depend on the $SiO_2/.Al_2O_3$ ratio and on the size of the crystallites. It is suggested that the sorptive properties of the pentasils may be influenced by various other factors which cannot be estimated by a simple analysis of the structure and composition of the zeolite, since they are determined by the previous history of the specimen[107]. They apparently include the nature of the localisation of the Al atoms in the crystal lattice, the phase purity of the zeolite, and the structural type to which it belongs (ZSM-5, ZSM-11, or a mixed structure).[70]

The chemical character of the adsorbate also has a significant influence on the nature of the sorption processes on pentasils. For example, ethylene and propylene, unlike ethane and propane, are adsorbed irreversibly and in larger quantities on the H-forms of ZSM-5 zeolites[103,107,122,123]. Infrared spectroscopy and other methods have shown that on pentasils, ethylene molecules are chemisorbed, activated, and react with other molecules of this alkene from the gas phase, forming a linear oligomer, which fills the pores of the zeolite[103,107,123]. When propylene is adsorbed, molecules of non-branched macromolecular compounds again accumulate in the pores of the pentasil. It is suggested that propylene undergoes conjugated polymerisation, and not oligomerisation, which leads to the formation of oligomers with quaternary carbon atoms, whose formation is prevented by the small diameter of the channels in the pentasil[122].

The formation of macromolecular compounds in the pores was also observed in a study of the adsorption of C_4–C_6 alkenes and cycloalkenes (cyclopentene, cyclopentadiene, and cyclohexene) on HZ-79 zeolite, an analogue of ZSM-5 zeolite[123]. In contrast to this, an infrared spectroscopic study of the adsorption of hex-1-ene, hept-1-ene, and cyclohexene on H-ZSM-5 zeolite detected only the interaction of the alkenes with the active (acidic) centres of the zeolite[124].

Because of the low concentration of Al atoms, the centres active in catalysis and adsorption are evidently situated at comparatively large distances from one another, and this lowers the probability of interaction between the sorbed molecules.

With increase in temperature, the oligomers or polymers filling the pores of the pentasil undergo cracking, and their decomposition products are readily removed as various hydrocarbons from the channels by a stream of inert gas[122,123]. In this way it has been possible, for example, to regenerate TsVK zeolite modified by added vanadium, which had been completely deactivated in experiments with ethylene by its oligomerisation products[125].

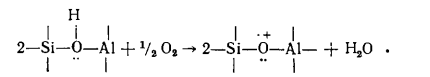
The sorption and catalytic properties of zeolites are due to the presence of active centres on their surface. It is therefore necessary to examine the question of the nature of these centres in pentasils and to determine whether there are any differences in this respect between pentasils and first-generation zeolites. Studies by infrared spectroscopy, mass spectrometry, and various other methods have shown[78,126-129] that the surface of pentasils, like that of first-generation zeolites[130], is covered by OH groups of two types. In the infrared spectra these correspond to two bands in the hydroxyl group stretching region at 3720 cm^{-1} and 3600 cm^{-1}.

The band at 3720 cm^{-1} is assigned to silanol or terminal OH groups (Si–OH), which do not have acidic properties and play no part in catalysis[78,130]. It is suggested[78] that these groups may also be joined to the amorphous SiO_2 present as impurity in pentasils. A recent study of the infrared spectra of a series of carefully prepared specimens of H-ZSM-5 zeolite with a high purity and different concentrations of Al atoms in the lattice (from 0 to 47 Al atoms in the unit cell) showed that the band at 3720 cm^{-1} is in fact due to a small quantity of structureless silicon dioxide, and also a very small quantity of terminal OH groups. Thus the presence or absence of this band in the infrared spectra of pentasils can be used as an indicator of the degree of crystallinity and the phase purity of the zeolite[131].

The band at 3600 cm^{-1} is due to acidic groups formed by the decationation of the Na- or NH_4-forms of the zeolites. It is usually assumed that they act as Brönsted acidic centres and are responsible for the catalytic activity of zeolites in acidic reactions[78,126-130]. These groups are joined to three-coordinate Al atoms in the zeolite framework (Si–OH–Al); the number of groups should therefore correspond to the concentration of Al in the crystal lattice. The infrared spectra of very pure specimens of H-ZSM-5 zeolite contain only the band at 3600 cm^{-1}.[131] Its width indicates that the acidic OH groups are apparently localised in cavities formed by the intersection of the channels of the pentasil.

The activation of zeolites at increased temperatures (T_{act}) is accompanied by the removal of both terminal and acidic (bridging) OH groups. As a result of dehydroxylation, the Brönsted acidic centres are converted into Lewis centres[130]. In first-generation zeolites, Brönsted centres can be regenerated by hydrating the dehydroxylated zeolites. In contrast to this, repeated hydration of an H-ZSM-5 zeolite activated at $T_{act} = 800°$ does not lead to regeneration of the Brönsted centres[78]. At a high T_{act}, apparently, a certain fraction of the Al atoms is removed from the zeolite framework and prevents the hydration of the Lewis centres, localised in the depth of the channels of the pentasil. This migration of aluminium as Al^{3+} cations from the framework of zeolites of type Y, and, to a lesser extent, mordenite was observed by ^{27}Al NMR spectroscopy after thermochemical treatment of the specimens[129,132]. It is assumed that the strong electron-acceptor properties of the Al^{3+} cations and the possibility of the heterolytic ionisation of water molecules in the field of these cations lead to the production in zeolites of type Y and mordenite of strong proton-donor centres of the type $[Al-O-Si]_3^-[O-Si].Al_3^+(OH)^-...H^+$. Since in zeolites of the TsVK type and erionite the migration of Al could not be detected, the authors cited[129,132] assumed that in these zeolites such centres are either absent or present at very low concentrations. It should also be noted that there are no published data confirming the existence of proton-donor centres of this type in zeolites.

Recent EPR data[133] indicate that the activation of pentasil at $T_{act} \geq 500°$ is accompanied by the conversion of Brönsted acidic centres into "solid state defects":



In the opinion of the authors[133], organic molecules adsorbed on a pentasil surface and capable of ionisation can react with these defects to form radical-cations, which undergo subsequent transformations. The reactions of this kind examined include the isomerisation of 3,3-dimethylbut-1-ene to 2,3-dimethylbutene, and the cyclotrimerisation of 1,2-dimethylacetylene.

As already noted, the quantity of Al atoms in the pentasil framework is much smaller than that in first-generation zeolites. Thus the concentration of Brönsted (and correspondingly Lewis) acidic centres in pentasils should be appreciably lower[78]. This is confirmed by data obtained by H–D exchange and from the infrared spectra of pyridine adsorbed on the zeolites (Table 1),[128] and also by ^{27}Al NMR spectroscopic data[129].

Table 1. Comparison of the acidic properties of H-ZSM-5 and HNaY zeolites[128].

Parameters	H-ZSM-5	HNaY
T_{act}, °C	400	500
Concentration of OH groups*	$2.2 \cdot 10^{20}$	$8.7 \cdot 10^{20}$
Concentration of Brönsted centres**	$3 \cdot 10^{19}$	$3 \cdot 10^{20}$
Concentration of Lewis centres	$2 \cdot 10^{19}$	$3 \cdot 10^{20}$

*Calculated for 1 g of zeolite (from H–D exchange data).
**The concentration of acidic centres in 1 g of zeolite was calculated from the infrared spectra of adsorbed pyridine.

The number of Brönsted acidic centres in the unit cell should correspond exactly to the number of Al atoms in the crystal lattice of the zeolite[131,132]. The calculation of the number of these centres in pentasils from the heats of adsorption of NH_3 (q), however, gives low values, and this has been attributed to the existence in the pentasils of very weak acidic centres ($q \leq$ ~60 kJ $mole^{-1}$), which cannot be detected by this method[78].

At the same time, the high acidity of the pentasils is combined with a comparatively low concentration of acidic centres. This suggested that these zeolites contain centres having an anomalously strong acidity. The microcalorimetric determination of the heats of adsorption of NH_3 revealed the existence in pentasils of acidic centres of different strength (acidity spectra);[132,134-137] however, only a very small proportion of the centres adsorbed ammonia with q ~150 to

160 kJ mole^{-1}, which was slightly greater than the corresponding value for zeolites of type Y and mordenite (120 to 140 kJ mole^{-1}).[132-137] Zeolites of the ultrasil and mordenite type showed practically no difference from one another in the heats of adsorption of NH_3 on the strongest centres (q ~ 150 kJ mole^{-1}).[134]

The infrared spectra of pyridine adsorbed on H-ZSM-5 showed that with increase in T_{act} from 500° to 800°, the intensity of the bands at 1550 cm^{-1} and 1460–1450 cm^{-1} in these spectra decreases, that is there is a decrease in the concentration of both the Brönsted and the Lewis centres[78]. An EPR study of the adsorption of NO, however, indicated that the number of the strongest Lewis centres, capable of adsorbing nitric oxide, begins to increase sharply at T_{act} > 500°.[78] The discrepancy in the data obtained by the two methods is apparently due to the greater accessibility of the strongly acidic centres of the zeolite for NO molecules, compared with pyridine. Moreover, these data also indicate that such centres are localised inside the pores of the zeolite[72,80,119,137]. Data on the acidic properties of ZSM-5 zeolite are also given in Ref. 138.

The published data on the hydroxyl covering and the acidic properties of Soviet pentasils of the TsVK type and ultrasil[84,134,139-147] agree with and supplement available data for ZSM-5 zeolites. For example, the highly sensitive infrared diffuse reflectance spectroscopy[145] confirmed the above data[78] on the existence of two types of OH group on the pentasil surface, and showed that high-temperature activation leads to the removal of OH groups from the zeolite surface, and that at T_{act} ≅ 900–1000°, some Al atoms migrate from the pentasil framework. These results[145] show good agreement with data obtained by H–D exchange[84], which show that there is an almost two-fold decrease in the concentration of the surface OH groups in a TsVK zeolite with increase in T_{act} from 300° to 700° (curve *1* in Fig. 5). It should be noted that the removal of this quantity of OH groups had practically no influence on the catalytic properties of the zeolite in the transformations of lower alkenes (isobutene): both the total yield of liquid products and the yield of aromatic hydrocarbons remained unchanged (curves *2* and *3* respectively in Fig. 5). Even the activation of the zeolite at 900 to 1000° has little influence on its total activity, although the ability of the zeolite to bring about dehydrocyclisation decreased appreciably. The catalytic activity of TsVK pentasil is apparently due to a small quantity of OH groups present in the active centres, which may break down only at T_{act} > 800°. After high-temperature treatment, the zeolite also showed a significant increase in selectivity in the formation of *p*-isomers of dialkylbenzenes, and this was attributed[84] to slight changes in the zeolite structure at high temperatures. These changes possibly involve the removal of Al atoms from the zeolite framework[145], lead to a decrease in the pore diameter, and create hindrance for the diffusion of molecules larger than *p*-dialkylbenzene molecules.

A number of other studies have established a relationship between the acidity and catalytic activity of pentasils[135,142,143,148,149]. For example, it has been shown[143] that a decrease in the number of strongly acidic centres in a zeolite of the ultrasil type by dehydroxylation is accompanied by a sharp decrease in the activity of this zeolite in the cracking of n-octane and iso-octane. According to Ref. 148, the rate constant for the transformation of methanol into hydrocarbons increases linearly with increase in the acidity (that is the number of acidic centres) of a catalyst based on a ZSM-5 zeolite. A correlation has been established between the acidity and the catalytic activity of H-ZSM-5 pentasil in the cracking of cumene, the isomerisation of *o*-xylene, and the decomposition of methanol and ethanol[149]. The number and strength of the acidic centres in the H-form of this zeolite depend on the conditions of its preparation from the NH_4-form.

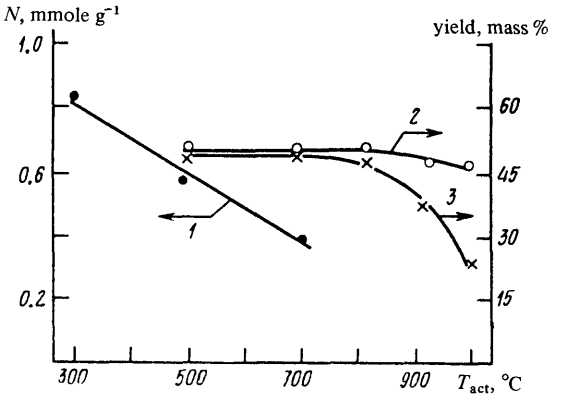


Figure 5. Dependence of the concentration of OH groups (N) in TsVK zeolite (*1*) and the yield of liquid catalysate (*2*) and aromatic hydrocarbons (*3*) from isobutene (500 °C) on T_{act}.[84]

Thus the composition and structure of the pentasils determine a number of specific properties which distinguish them from first-generation zeolites. These properties include, in particular, their hydrophobic nature, high thermal stability, and configurational molecular-sieve selectivity. The surface of the pentasils, like that of zeolites of any other type, carry hydroxyl groups, some of which show acidic properties, and apparently act as the source of the catalytic activity, playing the part of Brönsted acidic centres. The concentration of these centres in pentasils is appreciably lower than that in first-generation zeolites. Nevertheless, they show a high activity as catalysts in a whole series of reactions, and differ from zeolites of other types in their high stability. Data on the use of pentasils as catalysts in various reactions are examined below.

III. TRANSFORMATIONS OF OXYGEN-CONTAINING COMPOUNDS ON PENTASILS

1. Transformations of Methanol

The transformations of various oxygen-containing compounds, including methanol, on first-generation zeolites (chiefly of types X and A) have been the subject of a number of studies and reviews[38,40,42,150,151]. On these zeolites, methanol decomposes to give water, dimethyl ether, and small quantities of lower alkenes and alkanes; the catalysts rapidly lose their activity as a result of coke formation. In contrast to this, on ZSM-5 pentasils, methanol at 350–400° is completely converted into water (~56%) and a mixture of hydrocarbons (~44%).[28,32-37]

According to Ref. 152, the mixture of hydrocarbons formed from methanol contained propane (~16%), n-butane and isobutane (~25%), isopentane (~8%), aliphatic C_6–C_{10} hydrocarbons (~4%), and also toluene (~10%), xylenes (~17%), and

C_9 and C_{10} alkylbenzenes (~11%). The fact that the reaction products did not contain molecules with more than 10 carbon atoms was attributed to the influence of the porous structure of the zeolite, responsible for its molecular-sieve selectivity, as discussed above. This selectivity was also revealed in an increased concentration in the products, compared with the equilibrium concentration, of durene and isomers of tri- and tetramethylbenzenes, whose molecular size enabled them to diffuse comparatively easily from the pores of the zeolite into the gas phase.

The compositions of the products of the transformations of methanol on pentasils have also been studied in detail by other authors[87,138,149,153–167]. In addition to the hydrocarbons indicated above, these products contained small quantities of C_5–C_7 cyclanes and cyclenes, naphthalene, and alkylnaphthalenes[154,156,157]. Data on the composition of the products of the transformations of methanol on pentasils under similar conditions are given in Table 2.

Table 2. Characteristics of the transformations of methanol on ZSM-5 zeolite and the composition of the products.

Parameters of the process[1]	[152]	[153–154]	[155]	[156][3]	[87][3]	[157][4]	[158]	[159]
T, °C	370	350	370	370	400	340–360[5]	400	380
v, h^{-1}	1.0	1.0[6]	0.8	1.0	3.0	1.6	1.0	—
α, %	100	100	99	100	100	—	100	100
w, mass %	44	44	45	43	—	—	44	—
Hydrocarbon composition, mass %								
Aliphatic hydrocarbons, total:	58.8	73.3	55.6	71.8	21.6	63.8	84.7	47.0
including:								
C_1	1.0	—	41.3	0.9	2.9	2.1	0.7	3.0
C_2	1.1	3.2		5.1		1.3	3.6	11.0
C_3	17.2	20.4		9.0	10.3	11.7	10.8	13.0
C_4	25.6	26.7		21.8	8.4	14.9	29.7	20.0
C_5	9.6	13.2[7]	14.3	15.5[7]	traces	13.8[7]	39.9	
C_6–C_{10}	4.3	9.8[8]		19.5[8]	traces	20.0[8]		
Aromatic hydrocarbons, total:	41.2	26.7	44.4	28.2	78.4	31.6	15.3	45.0
including:								
benzene	1.7	1.4	41.8	—	traces	0.4	—	2.0
toluene	10.5	6.4		1.4	4.9	4.4	—	15.0
xylenes	17.2	13.4		6.1	73.5	12.2	—	28.0
ethylbenzene	0.8			0.2		0.9	—	
C_9 alkylbenzenes	7.5	5.5		9.7		10.8	—	
C_{10} alkylbenzenes	3.3	—		5.4		6.6	—	—
C_{11}+ alkylbenzenes	0.3	—	2.6	5.4[9]		0.9[9]	—	—

[1] T = temperature, v = volume flow rate, α = degree of transformation, w = yield of hydrocarbons.

[2] Pilot plant, fluidised-bed catalyst, N_2 carrier gas.

[3] Pilot plant, stationary catalyst layer, H_2 carrier gas.

[4] After 73 h catalyst use without regeneration in a pilot plant.

[5] Temperature at reactor inlet; temperature at outlet 404°.

[6] Calculated for the pure zeolite, mixed in the catalyst with SiO_2 (1:1).

[7] Including C_5 naphthenes.

[8] Including C_6 and C_7 naphthenes.

[9] Including naphthalene and alkylnaphthalenes.

In spite of the significant differences in the conditions of these reactions (in laboratory[87,152–154,158] or pilot-plant[155–157] assemblies with stationary or fluidised-bed[156] layers of catalyst) and the fact that different ZSM-5 zeolite specimens were used, the data in Table 2 show considerable agreement. Thus in all cases the conversion of the alcohol is ~100%, the yield of hydrocarbons is stoichiometric (~44%), and the products contain 1–3% methane and an appreciable quantity of alkanes, in which iso-alkanes predominate. At the same time, appreciable differences are observed in the distribution of individual products and in the ratio of the quantities of aliphatic and aromatic hydrocarbons formed. Thus the composition of the products of the transformation of methanol depends on the reaction conditions (temperature, volume rate, pressure) and on the composition of the catalyst (the SiO_2/Al_2O_3 ratio).

In a flow reactor with a stationary catalyst layer (H–ZSM-5), the conversion of methanol increased rapidly with temperature, and reached 100% at 340–375°.[152] Below 300°, methanol was converted chiefly into dimethyl ether with the formation of small quantities of C_2–C_5 alkanes and alkenes (7–10%) and aromatic hydrocarbons (~1–3%). At 300–400° the products contained only aliphatic and aromatic hydrocarbons (60% and 40% respectively). Increase in temperature to 450–500° led to the formation of methane and lower alkanes by secondary cracking reactions, and above 500°, methanol decomposed directly to CO and H_2.

Analogous results were obtained when other H-ZSM-5 zeolite specimens were used[153–155,158], including specimens with added phosphorus[158]. With a fluidised-bed catalyst based on ZSM-5 zeolite[156], the reaction rate increased by a factor of 1.5 for each increase in temperature by ~27–30 K. The influence of temperature on the distribution of the products of the transformation of methanol on H-ZSM-5 zeolite was studied in detail[124], and the results showed good agreement with earlier data[152].

The transformations of methanol on ZSM-5 zeolites at different volume rates have been studied[152,154,156,160,163,168]. Increase in the volume rate (v) by a factor of more than 1000 (from 1 h^{-1} to 1080 h^{-1}) lowers the conversion of methanol (370°, p_{CH_3OH} = 1 atm) by a factor of approximately 3 (from 100% to ~30%) and has a significant influence on the direction of the transformations of the alcohol[152]. The change in the composition of the products of the transformations of methanol with change in the volume rate for different partial pressures of alcohol (p_{CH_3OH}) is shown in Figs. 6*a* and 6*b*.[152,160] These data also indicate that p_{CH_3OH} influences the composition of the products formed from methanol on ZSM-5 zeolites. Increase in p_{CH_3OH} leads mainly to an increase in the selectivity of the process with respect to the formation of polyalkylbenzenes, in particular durene[155,156,160]. Thus the aromatic fraction of the products formed from CH_3OH on H-ZSM-5 zeolite at p_{CH_3OH} = 1 atm (370°, v = 1 h^{-1}) contains only ~2 mass % durene[152], whereas at p_{CH_3OH} = 50 atm under the same conditions, the durene concentration increases to ~60 mass %.[160] It is suggested[160] that polyalkylbenzenes are formed by alkylation taking place with simultaneous dehydration of the oxygen-containing compounds and aromatisation of the hydrocarbons (hatched region in Fig. 6*a*). With increase in p_{CH_3OH}, this range broadens considerably (Fig. 6*b*), leading to an increase in the range of conditions favouring the formation of polyalkylbenzenes. With decrease in p_{CH_3OH} to 0.04 atm, the range corresponding to simultaneous dehydration and aromatisation practically disappears, and polyalkylbenzenes are formed in very small quantities.

The degree of transformation of methanol and the composition of the reaction products depend to a significant extent on the SiO_2/Al_2O_3 ratio and the concentration of Na in the pentasil. In the transformation of methanol (400°, v = 3 h^{-1}) on the original form of silicalite (0.22 mass % Na,

SiO_2/Al_2O_3 = 1125), the initial conversion of alcohol was ~50%, and the reaction products contained chiefly dimethyl ether and a small quantity of propane[87]. With decrease in the concentration of Na in the silicalite, the conversion of methanol gradually increased to 100%, and the resulting mixture of aliphatic and aromatic hydrocarbons showed an increased concentration of arenes (up to ~45 mole %). The original and decationated forms of ZSM-5 zeolite were much more active in the transformations of methanol, although the concentration of Na in them (2.03 mass % and 0.38 mass % respectively) were much higher than in the original form of silicalite. In both cases the conversion of the alcohol was 100%. As with silicalite, decrease in the concentration of Na in the zeolite was accompanied by an increase in the concentration of aromatic hydrocarbons in the reaction products (from 20 mole % to 78 mole %).

Thus to obtain silicalite specimens active in the transformation of methanol, it is necessary to have much more extensive decationation than with ZSM-5 pentasil, which is active even in the Na-form. Thus the lower the Al concentration in the zeolite, the greater the extent to which its catalytic activity is suppressed by sodium.

The influence of the SiO_2/Al_2O_3 ratio on the catalytic properties of H-ZSM-5 zeolite in the transformations of methanol can be judged from the published data[161] in Table 3. For the zeolite specimens *1* and *2* with SiO_2/Al_2O_3 ratios of 38 and 54.5 respectively, the conversion of the alcohol and the composition of the reaction products were practically the same, in spite of the difference in the Na concentration in the zeolites and the difference in the reaction temperatures. Increase in this ratio to 158 (specimen *3*), however, decreased the conversion of the alcohol by a factor of almost 2, and in this case the alcohol was converted chiefly into dimethyl ether. Thus the activity of ZSM-5 zeolites in the transformation of methanol into hydrocarbons depends on the concentration of Al atoms in the zeolite framework. Below a definite concentration of these atoms (~0.5%), the number of active centres in the zeolite evidently becomes insufficient for the formation of hydrocarbons from methanol.

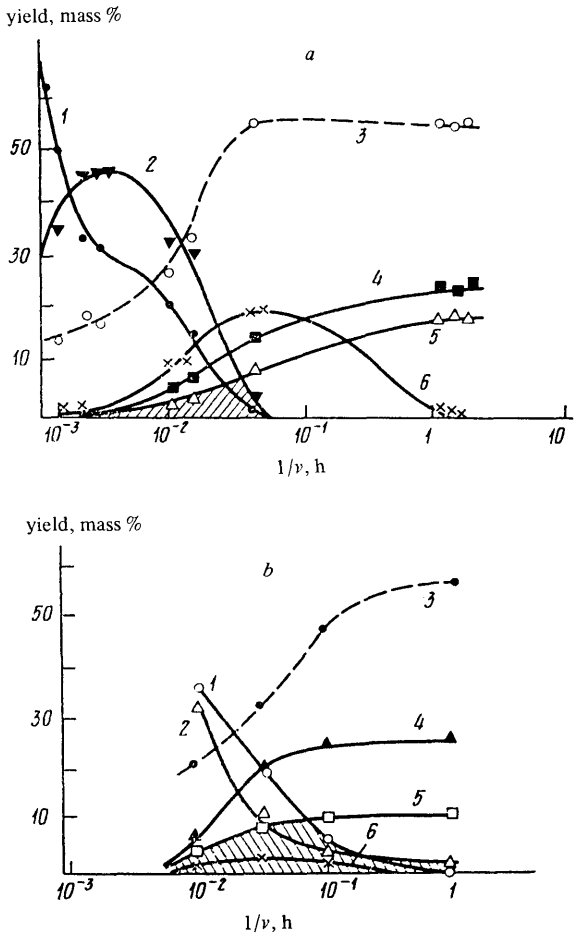


Figure 6. Dependence of the composition of the products of the transformation of methanol on H-ZSM-5 zeolite (370 °C) on the reciprocal of the volume flow rate at $p_{CH_3OH} = 1$ atm (*a*) and 50 atm (*b*): [*1*) CH_3OH; *2*) $(CH_3)_2O$; *3*) H_2O; *4*) alkanes; *5*) aromatic hydrocarbons; *6*) C_2–C_5 alkenes].[160]

Table 3. Transformations of methanol on H-ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios.

Parameters of the process	H-ZSM-5 zeolite specimens		
	1	2	3
x	38	54.5	158
[Al], %	2.16	1.51	0.53
[Na_2O], mass %	0.05	0.10	0.15
T, °C	372	380	372
v, h^{-1}	10	11	11
α, %	89	89.7	48.6
Composition of products, mass %			
Methanol	11.0	10.3	51.4
Dimethyl ether	7.8	10.6	44.9
Hydrocarbons, total:	81.2	79.1	3.7
including: aromatic	9.1	5.4	0.5
aliphatic	90.9	94.4	99.5

In an examination of the relationship between the composition of pentasils and their activity in the transformations of methanol, mention must be made of patent data[23,24,28,30,169,170], according to which modification of ZSM-5 zeolites by the addition of various elements (Mg, B, Zn, Cd, Sb, Ni, Pd, P, etc.) leads to an increase in the yield of liquid products from methanol and to an increase in the concentration of aromatic hydrocarbons in them. Treatment of a ZSM-5 zeolite with various phosphorus compounds (for example trimethyl phosphite) lowers slightly its activity in transformations of methanol, but increases the selectivity of the reaction with respect to the formation of ethylene and other lower alkenes, particularly at low temperatures[158]. After this treatment, the zeolite showed an increase in the quantity of acidic centres, but these centres were weaker than the centres of the non-modified pentasil[158].

An increase in the selectivity of the transformations of methanol with respect to C_2 and C_3 alkenes was also detected[171] on MnNa-ZSM-5 and MgNa-ZSM-5 zeolites prepared by cation exchange. These zeolites are more stable than MnNaY and MnNaX zeolites.

The production of ethylene and propylene from methanol with a good selectivity (more than 75%) was observed on non-modified ZSM-34 pentasil[6]. This catalyst rapidly lost its activity, however, as a result of coke formation. Improvement of the method of synthesis of ZSM-34 zeolite by using seed crystallites led to a significant change in its catalytic properties. The total yield of hydrocarbons from methanol at 400° increased by a factor of ~2, the selectivity with respect to C_2 and C_3 alkene formation increased to ~80%, and the time of service of the catalyst increased by a factor of 2.2.[172,173] These positive effects are due to the high uniformity of the size and shape of the zeolite crystallites formed in the presence of the seed crystals. Detailed information on the influence of the nature and quantity of added seed crystals on the structural, catalytic, adsorptive, and other properties of ZSM-34 zeolite has been published[174,175]. On the basis of this zeolite, synthesised using a seed crystal, a technical process has been proposed for converting methanol into C_2–C_4 alkenes with a selectivity of more than 86%.[176]

Comparison of the products of the transformation of methanol on H-ZSM-5 and H-ZSM-11 pentasils[113] showed that on H-ZSM-5, aromatic C_8 hydrocarbons are formed preferentially, whereas on H-ZSM-11, more C_9 hydrocarbons are obtained. These results[113] were attributed to differences in the volume of the cavities formed at the intersections of the pores in zeolites of these two types. It was also established that the products of the transformations of CH_3OH on large crystallites of H-ZSM-11 zeolite have approximately the same composition (more aliphatic C_1 and C_2 hydrocarbons, less C_6 hydrocarbons and aromatic C_9 hydrocarbons), as on H-ZSM-5 crystallites with the same size.

The low degree of coke formation characteristic of pentasils, and the corresponding high stability of operation as catalysts, also depend on the composition of the zeolite. Na silicalite and Na-ZSM-5 zeolite are deactivated completely after use for 5 h under the conditions of methanol transformation at 400°.[87] Under the same conditions, the activity of decationated silicalite remains unchanged for ~6 h, and H-ZSM-5 zeolite is not deactivated after ~12 h.

It should be emphasised again that the high stability of pentasils is due primarily to their unusual porous structure[112,117,118]. A study of the transformations of methanol on H-ZSM-5 zeolites, H-offretite, and H-mordenite[119] showed that the maximum quantity of coke deposited on these catalysts after use for 12 h at 380° increased in the order H-ZSM-5 < H-mordenite < H-offretite, and amounted to 2.2, 8.7, and 16.8 mass % respectively. H-mordenite and H-offretite are almost completely deactivated after 30 min and 55 min respectively, whereas the activity of H-ZSM-5 zeolite decreased only slightly after this catalyst had been used for 1.5 h. For all three zeolites, increase in the quantity of coke formed was accompanied by various changes in the distribution of the hydrocarbons formed. For example, for H-ZSM-5 zeolite the ratio C_4H_{10}/C_4H_8 gradually decreased, approaching a constant value. Simultaneously, the products showed an increase in the already high concentration of *p*-xylene. Overall, the ratio of the concentrations of *p*-xylene and *o*-xylene for H-ZSM-5 zeolite reached values >40, whereas for the other two zeolites it was 0.5–2.0 and remained unchanged throughout the experiment. EPR showed that the coke deposited on H-ZSM-5 has a low hydrogen content, and is similar to graphite in character. In contrast to this, the coke on H-mordenite, and H-offretite corresponds more to polynuclear atomatic systems. It was suggested[119] that as a result of the size and shape of the channels in H-ZSM-5 zeolite, coke formation takes place chiefly on the outer surface of the zeolite and does not influence the strongly acidic centres which are localised within the pores and which are responsible for the catalytic activity. The surface coke may partly block the entry to the pores, however, increasing the molecular-sieve properties of the pentasil, as revealed by the change in the selectivity of the process during the operation of the catalyst.

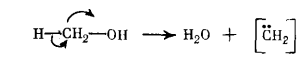
H-ZSM-5 zeolite has a high stable activity under the conditions of the formation of aromatic hydrocarbons from methanol under pulse conditions (450 °C), whereas the new SHS zeolite Nu-1 ($SiO_2/Al_2O_3 \cong 53$), whose structure does not correspond to the pentasil family, is rapidly deactivated by coke formation[177].

Considerable attention has been paid to the study of the stability of catalysts based on H-ZSM-5 zeolite in the development of a technical process for producing petrol from methanol in pilot plant[155–157]. By carrying out the stage of alcohol dehydration and the stage of the production of a mixture of hydrocarbons from the dehydration products in two different reactors with a stationary layer of zeolite catalyst[155], it was shown that the deactivation of the latter takes place predominantly in the second stage as a result of coke formation. The period of use of this catalyst in the second stage without regeneration reached 167 h, and after this period a significant change in the selectivity of the process was observed: the yield of C_3 and C_4 alkenes and hydrocarbons containing five and more carbon atoms decreased. The results were confirmed under prolonged testing conditions, in which ten working cycles with a total duration of ~207 d were carried out without replacing the catalyst. Under fluidised-bed conditions, a catalyst based on ZSM-5 zeolite functioned for more than 50 d. During this time it was regenerated six times using air[156]. In each working cycle the high initial activity of the catalyst gradually decreased with time, and after each regeneration the activity of the catalyst at the start of the next cycle was lower than that at the start of the previous cycle.

2. Mechanism of Formation of Hydrocarbons from Methanol

The intensive study of the transformations of methanol to hydrocarbons on the new generation of zeolites has led to the development of earlier[178–180] suggestions about the mechanism of this process.

From the ideas of Venuto and Landis[179] on the mechanism of the decomposition of methanol on zeolites of type X, it was suggested[152] that on ZSM-5 zeolites, methanol or its decomposition product dimethyl ether can decompose to give carbene-like methylene biradicals



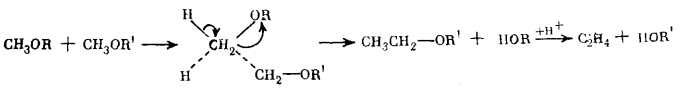
These biradicals may then either dimerise

$$2\,[\ddot{C}H_2] \rightarrow C_2H_4$$

or react with molecules of methanol or dimethyl ether

$$[\ddot{C}H_2] + CH_3OR \rightarrow CH_3CH_2{-}OR \xrightarrow{+H^+} C_2H_4 + HOR \quad (R = H,\ CH_3)$$

Since the molecules of alcohol or ether act as both donors and acceptors of methylene biradicals, this mechanism can be represented as a conjugated bimolecular reaction

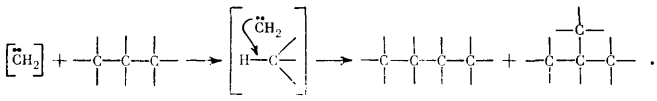


R and R' = H, Alk.

After the formation of the first molecules of alkene (ethylene), the carbene biradicals can add on across the double bond, giving hydrocarbons with higher molecular weight.

Later, on the basis of this mechanism, a kinetic model was developed[181] for the transformation of methanol to hydrocarbons on ZSM-5 zeolites, making it possible to determine with satisfactory accuracy the extent of the conversion of alcohol and the selectivity of the process over a wide range of pressures.

Because of the doubts expressed by various authors about the correctness of the carbene mechanism, data were published[182], which in the author's opinion proved that carbene biradicals are formed from methanol on ZSM zeolites. According to these data, in the transformations of $^{13}CH_3OH$ on H-ZSM-5 zeolite (370°, 1 atm, $v = 0.4\ h^{-1}$), dilution of the alcohol by propane (whose conversion under these conditions is ~0.3%) decreases by a factor of more than three the ratio of isobutane to n-butane in the reaction products compared with experiments in which methanol was diluted with helium. The data on the distribution of the ^{13}C isotope between the butane isomers formed made it possible to attribute this effect to the direct methylation of the "inert" propane by carbene biradicals. The reaction can take place by the introduction of this biradical at one of the sp^3 C–H bonds of propane



This reaction should give 75% n-butane and 25% isobutane, which corresponds to the results obtained.

One objection to the carbene mechanism is that it does not explain the formation from methanol of methyl ethyl ether and large quantities of isoalkanes, and the increase in the yield of alkenes with decrease in the conversion of alcohol[153,154]. The authors cited suggested that on ZSM-5 zeolites, whose surface has strong Brönsted acidic centres, methanol may undergo dehydration, being converted successively to dimethyl ether and ethylene[178,180]

$$2CH_3OH \xrightarrow[-H_2O]{} CH_3OCH_3 \xrightarrow[-H_2O]{} CH_2{=}CH_2 .$$

According to this scheme, methanol should be converted chiefly to ethylene, which does not agree with data on the composition of the products on the transformation of this alcohol, which contain only small quantities of ethylene (see Table 2). It was therefore suggested that ethylene is highly reactive and readily forms carbenium ions by reacting with Brönsted acidic centres

$$CH_2{=}CH_2 + HOZ \rightarrow CH_3\overset{+}{C}H_2 \cdots \bar{O}Z .$$

The reaction can then proceed in two directions

$$CH_3\overset{+}{C}H_2 \cdots \bar{O}Z \left\{ \begin{array}{l} \xrightarrow[a]{CH_3OH} CH_3CH_2{-}O{-}CH_3 + HOZ \\ \xrightarrow[b]{CH_2=CH_2} CH_3CH_2CH{=}CH_2 + HOZ . \end{array} \right.$$

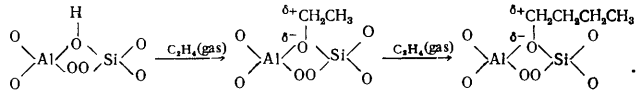
Path *a* gives methyl ethyl ether, which can be dehydrated to give propylene

$$CH_3CH_2{-}O{-}CH_3 \rightarrow CH_3CH_2{=}CH_2 + H_2O .$$

Propylene ether is converted into propane by redistribution of hydrogen, or, like ethylene, reacts with Brönsted acidic centres (path *a*) giving a more stable secondary carbenium ion, leading to the formation of iso-alkanes.

The linear hydrocarbons which are formed according to path *b* by polymerisation, and which contain not less than six carbon atoms, can then undergo cyclisation to give aromatic hydrocarbons. According to the proposed mechanism, the development of the process in the system requires the continuous presence of unconverted methanol. It is therefore suggested that in addition to the forward reaction of alcohol dehydration, the back reaction of alcohol formation also takes place, and both of these reactions compete with the processes of polymerisation, cyclisation, and aromatisation.

To confirm the carbenium-ion mechanism, the adsorption of ethylene on dehydrated H-ZSM-5 zeolite was studied[103]. Thermogravimetric and ^{13}C NMR and infrared spectroscopy indicated that on the strong Brönsted acidic centres of the zeolite, low-temperature chemosorption and activation of ethylene can take place according to the scheme



The addition of ethylene to OH groups corresponds to the formation of carbenium ions, which take part in chain growth giving macromolecular aliphatic hydrocarbons capable of undergoing isomerisation and aromatisation at higher temperatures (300–400°).

In a study of the transformations of methanol on H-ZSM-5 zeolite in the presence of carbon monoxide[183], ^{13}C NMR spectroscopy showed that the products contained saturated and unsaturated aliphatic (and aromatic) aldehydes and ketones. Their formation is attributed only to the reaction of CO with carbenium ions present on the surface

$$CH_3\overset{+}{C}H_2 + CO \rightarrow CH_3CH_2{-}\overset{+}{C}O \xrightarrow{\text{alkane}} CH_3CH_2CHO ,$$
$$CH_3CH_2CHO + C_2H_4 \rightarrow CH_2{=}CH{-}CHO + C_2H_6 .$$

These data also indicate the impossibility of the formation of carbenium biradicals, which in the reaction with CO should give ketene, capable of reacting with the water, methanol, and ethylene present in the system. No products of these reactions (acetic acid, its methyl ester, and cyclobutane) were detected.

These results[103,153,154,183] made it possible to develop a detailed scheme for the transformations of methanol to various hydrocarbons on pentasils with the participation of carbenium ions[166]. According to this scheme, the reaction of carbenium ions with various components of the reaction system can give a broad spectrum of aliphatic and aromatic C_6–C_{10} hydrocarbons, including appreciable quantities of xylenes, ethylbenzene, and 1,2,3-trimethylbenzene. It was subsequently shown[184] that aromatic hydrocarbons are formed predominantly on centres localised in the cavities formed at the intersection of the channels in the pentasils. Since the geometry of the pores in these zeolites permits the simultaneous dehydrocyclo-oligomerisation of only two aliphatic C_5 molecules, the aromatic hydrocarbons formed cannot contain more than ten carbon atoms.

A slightly different mechanism has also been proposed[185], according to which not ethylcarbenium but methylcarbenium (CH_3^+) ions, differing from carbenium biradicals, are formed from methanol on pentasils.

The presence of small quantities of ethylene in the products of the transformation of methanol on pentasils, and also the low degree of conversion and poor reproducibility of the results in experiments with this alkene, led to the suggestion[87] that ethylene is not highly reactive on these zeolites. Thus the role of active intermediate species in the formation of hydrocarbons from methanol is played not by ethylcarbenium ions but by "unsaturated C_3 and C_4 residues", as

shown in the scheme

$$CH_3OH \xrightarrow{H^+_{surf}} (\text{unsaturated } C_3 \text{ and } C_4 \text{ residues})_{surf} \begin{cases} \longrightarrow C_3 \text{ and } C_4 \text{ alkenes} \\ \longrightarrow \text{aromatic hydrocarbons} \end{cases}.$$

Here, H^+_{surf} is an acidic centre on the zeolite surface. To obtain more details of this scheme, the transformations of methanol and various hydrocarbons on H-ZSM-5 zeolite were studied using deuteriated compounds[186]. The results, with allowance for the reaction of methanol on Brönsted acidic centres, indicated that in the first stage of the reaction, activated species $(CH_3)\overset{+}{R}OH$ (R = H, CH_3) are formed on the zeolite surface. Simultaneously, methanol is dehydrated to give alkenes, in which the number of carbon atoms ≥3. This is followed by growth of the carbon chain according to the scheme

$$(CH_3)\overset{+}{R}OH_{surf} + R'R''C{=}CH_2 \rightarrow R'R''\overset{+}{C}{-}CH_2CH_3{}_{surf} \xrightarrow{+ROH} R'R''C{=}CHCH_3 + H^+_{surf}$$
$$R', R'' = H, Alk$$

Isomerisation and dehydrocyclisation, and also the rupture and formation of C=C bonds, can take place, depending on the temperature.

To supplement this mechanism, a scheme was proposed for the transformation of methanol to alkenes with the intermediate formation of methyl isopropyl ether with the subsequent elimination of methanol and the formation of propylene[187]. This scheme has been considered unlikely, however, since the size of the molecule of the intermediate compound is much greater than the diameter of the pores of the zeolite[188].

The formation of hydrocarbons from methanol on H-ZSM-5 zeolite, modified by phosphorus, has also been represented by a general scheme giving only the possible routes and the sequence of transformations of the alcohol[158]. In addition, it was suggested[158] that with a zeolite containing phosphorus, a significant part begins to be played by reactions, catalysed by the acidic centres, involving the alkylation of methanol by methanol (to give dimethyl ether), of ether by ether (to give methyl ethyl ether, which by the removal of an alcohol molecule gives ethylene), and of alkenes by methanol (chain growth). Oligomerisation of alkenes, cracking of oligomers, cyclisation, and hydrogen transfer may also take place.

The mechanism proposed in[189] assumes the formation of intermediate alkyloxonium ions $[R_3O]^+$, where R = H, CH_3, C_2H_5, etc., which can undergo intramolecular rearrangements. According to this mechanism, methanol is dehydrated to dimethyl ether, which on Brönsted acidic centres may be converted into the dimethyloxonium ion $[(CH_3)_2HO]^+$. The reaction of this ion with a dimethyl ether molecule gives an intermediate compound, and the removal of a methanol molecule from the latter gives the stable trimethyloxonium ion $[(CH_3)_3O]^+$. The C–H bonds in this ion may be polarised on the basic centres of the zeolite, formed by the deprotonation of the Brönsted acidic centres. The trimethyloxonium ion can then undergo rearrangement to the methylethyloxonium ion, which can give up a methanol molecule to form ethylene and regenerate the Brönsted acidic centre.

Simultaneously, the dimethyloxonium ion formed at the start of the process can react in six directions with the molecules of water, methanol, and dimethyl ether present in the system. This should lead to the predominant formation of ethylene, whose subsequent transformations give a whole spectrum of hydrocarbons, detected in the reaction products. In spite of its complexity, the mechanism involving alkyloxonium ions explains many experimental facts. Some authors suggest that the formation of hydrocarbons from methanol is autocatalytic[138,148,168]. In an isothermal system on catalysts containing 1.4–10% H-ZSM-5 zeolite and an inert diluent (γ-Al_2O_3 or metallic copper powder), it was shown[148] that at low CH_3OH concentrations the rate of consumption of alcohol is very low, but increases rapidly with increase in the concentration of the alkenes formed. The increase in the reaction rate is apparently due to the autocatalytic reaction of the original alcohol with the alkene (propylene) formed. Kinetic calculations showed that the rate constant of this autocatalytic stage of the process is 50 times the rate constant for the formation of the alkene from the alcohol[148].

The conclusion that the transformations of methanol on ZSM-5 zeolites is autocatalytic was also reached from data which showed a sharp increase in the rate of transformation of the alcohol when an alkene was introduced into the system[138] and data which showed an abrupt increase in the yield of hydrocarbons for a comparative small increase in the temperature of the reaction (from 280° to 300°).[168] It was suggested that the first stage of the process involves the reaction of methanol with a Brönsted acidic centre to give the methylcarbenium ion. The reaction of this ion with an alcohol molecule gives a proton and an ether, which decomposes to give ethylene

$$\overset{+}{C}H_3 + CH_3OH \rightarrow \left[\begin{matrix} H \\ CH_3 \end{matrix} \!\!>\!\! CH_2OR \right]^+ \rightarrow CH_3CH_2OR + H^+ .$$

Thus there is still lack of agreement about the mechanism of formation of hydrocarbons from methanol on zeolites of the new generation. At present, apparently, there is agreement only on the first stage of the process, involving the dehydration of the alcohol to dimethyl ether. There is lack of agreement about the mechanism of all the other stages, because of the lack of convincing proof. Up to the present, no unambiguous answers have been obtained to the questions of how the first C–C bond is formed from methanol (or dimethyl ether), and what is the nature of the resulting compound, which is the precursor of all the other hydrocarbons detected in the reaction products. The nature of the intermediate compounds involved in the development of the transformation of methanol into hydrocarbons is also not clear. According to existing ideas, these compounds may be carbene biradicals, carbenium ions, or alkyloxonium ions. The suggestion that intermediate carbenium biradicals are formed has been criticised[153,154,187,191], and these criticisms have been answered, and the suggestion clarified[188,192]. Thus it has been shown[188] that the decomposition of dimethyl ether or methanol can be represented by a scheme involving both carbenium biradicals and carbenium ions. It was concluded that the carbenium mechanism is to some extent provisional, and does not assume the existence of free carbenium biradicals.

It is at present difficult to give preference to any of the proposed mechanisms. The most reliable mechanisms, however, agreeing with current ideas on catalysis, are those involving carbenium ions.

3. Transformations of Other Oxygen-Containing Compounds

Alcohols. In addition to methanol, the transformations of various other alcohols, primarily ethanol, on pentasils have been studied. Comparison of the results of the most detailed study[154] of the products formed from ethanol on H-ZSM-5 zeolite (SiO_2/Al_2O_3 = 43.6; 0.05 mass % Na_2O) with the analogous data for methanol shows that C_2H_5OH undergoes transformations more readily than CH_3OH. Even at 250°, its conversion reached more than 99% (85% methanol), and the reaction products contained more than 98% hydrocarbons (2 to 11% in the case of methanol). At high rates of supply, ethanol is almost completely converted into ethylene[154]. Beginning at 300°, the formation of aromatic hydrocarbons

is observed, and the quantity decreases with increase in the rate of supply of the alcohol, but increases with increase in the reaction temperature. More ethylbenzene and ethyltoluene are formed from ethanol than from methanol. The start of the formation of aromatic hydrocarbons in the gaseous reaction products is accompanied by a sharp decrease in the ethylene concentration, but the concentration of C_4 alkanes and alkenes increases[154].

The formation of aromatic hydrocarbons from ethanol on H-ZSM-5 zeolite has also been observed[193]. The yield of aromatised products increases with increase in temperature (>260°), with decrease in the rate of supply of alcohol, and with the addition of water to the reaction mixture. Water prevents deactivation of the zeolite catalyst[193]. Unlike pentasil, dealuminated Y and M zeolites in the H-form showed only dehydrating properties, and H-mordenite rapidly lost its activity even in the presence of water.

H-ZSM-5 zeolites are deactivated more rapidly in the transformations of ethanol than in experiments with methanol[194]. In addition, ethanol gave more trimethylbenzenes and aromatic hydrocarbons with higher molecular weights, the quantity of which in the reaction products increased with deactivation of the zeolite. A study of the adsorption of n-hexane and toluene on H-ZSM-5 before and after the experiments showed that during use with ethanol, the sorptive capacity of the zeolite decreases, but it can be restored by regeneration in a stream of oxygen.

Ethanol has been transformed into ethylene with a high selectivity on the Na- and H-forms of ZSM-5 zeolite at 200 to 250°.[195] The products contained almost no diethyl ether, but contained acetaldehyde, the quantity of which increased with temperature.

Table 4. Composition (mass %) of the products of the transformations of various alcohols and dimethyl ether on H-ZSM-5 zeolites (for all compounds, $\alpha \cong 100\%$).

Products	Original compound					
	CH_3OH[1]	C_2H_5OH[2]	$t\text{-}C_4H_9OH$[1]	$C_7H_{15}OH$[1]	$(CH_3)_2O$[3]	$(CH_3)_2O$[3]
Methane	1.0	—	0.1	—	—	4.8
Ethane + ethylene	1.1	5.2	1.2	0.4	15.8[4]	15.2
Propane	16.2	10.8	18.8	16.4	11.1	23.4
Propylene	1.0	2.7	1.1	0.2	6.9	
Isobutane	18.7	17.9	18.4	19.3	8.6	16.0
n-Butane	5.6	5.9	8.6	11.0	4.3	
Butenes	1.3	6.6	0.7	0.1	10.0	
Isopentane	7.8	—	6.2	8.7	—	
n-Pentane + pentenes	1.8	18.3	1.6	1.6	14.6	
Hexane + hexenes	4.3	12.2	7.6	3.0	17.2	
Benzene	1.7	0.5	3.3	3.4	0.3	4.6
Toluene	10.5	3.5	11.6	14.3	1.2	12.0
C_8 alkylbenzenes	18.0	6.5	13.7	12.8	6.9	12.7[5]
C_9–C_{11} alkylbenzenes	11.0	10.1	7.1	8.8	3.4	—

[1]From published data[152] at 370°.
[2]From published data[189] at 310° after zeolite use for 28 min.
[3]From published data[159] under pulse conditions; 550°, TsVK zeolite.
[4]Only ethylene.
[5]Only xylenes.

At 350° under a pressure of 50 atm, ethanol on H-ZSM-5 zeolite gave quantities of durene smaller by a factor of 65 than those obtained from methanol, but the quantities of various alkylbenzenes (ethyl-, methylethyl-, dimethylethyl-, and diethylbenzenes) were ~7 times greater[160].

Thus the transformations of ethanol on pentasils show characteristic features, although the products of the transformations of ethanol and methanol have approximately the same composition (Table 4), in spite of the significant difference in the conditions of the reactions and in the pentasil specimens used[149,152,189]. The similarity in the products formed from the two alcohols has been noted by other workers[160,195]. It was therefore suggested[154,195] that the mechanisms of the transformations of ethanol and methanol on pentasils are the same, and involve the formation of carbenium ions on Brönsted acidic centres with the participation of ethylene, as the primary unsaturated hydrocarbon. According to another view[194], the ease of formation of C_9–C_{12} aromatic hydrocarbons from ethanol indicates that its molecules are split into C_2 fragments, whereas CH_3OH gives mainly C_1 fragments.

The transformations of alcohols with higher molecular weights than ethanol on pentasils have been described in only two papers[152,196]. The data for t-butyl, heptyl, and methyl alcohols (Table 4) show that the composition of the products is approximately the same in all cases[152]. Irrespective of the original alcohol, these products contain less than 1% methane, and the main products are propane, isobutane, toluene, and xylenes. The data for heptan-1-ol, however, were obtained at a lower volume rate ($0.7\ h^{-1}$), and this may indicate that this alcohol is less reactive than t-butyl alcohol and methanol.

A study of the transformations of 2-methylbutan-2-ol on TsVK pentasil and on zeolites of type Y (NaY, CaY, HY) [196] showed that at 120–200°, the alcohol decomposes to give 2-methylbut-1-ene, 2-methylbut-2-ene, and 3-methylbut-1-ene. The Na-form of the TsVK zeolites was more active than NaY, but less active than CaNaY and HNaY.

Simple ethers. Among these compounds, the transformations of dimethyl ether—the intermediate product in the formation of hydrocarbons from methanol on pentasils—have been studied in greatest detail. In most cases the experiments with dimethyl ether were carried out to investigate the mechanism of formation of the hydrocarbons from the alcohol[107,152,158,189]. In addition, the transformations of dimethyl ether have been used as a model reaction in the study of the influence of various factors on the catalytic properties of ZSM-5 zeolites[159,197] and in their comparison with the properties of amorphous aluminosilicate, prepared using organic bases[166].

Table 4 shows that the transformations of dimethyl ether on pentasils give (in addition to water and methanol) the same hydrocarbons as in the products of the transformations of methanol and other alcohols. In contrast to alcohols, the decomposition of dimethyl ether on ZSM zeolites gives considerable quantities of ethylene. It was therefore suggested[189] that it is ethylene that is the primary hydrocarbon in this process, and that its rapid methylation gives propylene. Data on the composition of the products of the transformation of dimethyl ether formed the basis of the mechanism, examined above, for the formation of hydrocarbons from methanol involving alkyloxonium ions[189].

The influence of the reaction conditions on the composition of the products formed from dimethyl ether has been studied[152,189]. At a temperature below 300°, the products contain chiefly C_2–C_5 alkenes, whereas at 350°, the formation of appreciable quantities of aromatic hydrocarbons (~20 mass %) and also C_2–C_5 alkanes (~20 mass %) is observed. The nature of the dependence of the conversion of dimethyl ether and the composition of its transformation products on the reciprocal of the volume rate agrees satisfactorily with the

analogous data for methanol (see Fig.6). Similar results were obtained on H-ZSM-5 zeolite modified with phosphorus[158].

Pentasils show a slightly lower stability under the conditions of the transformations of dimethyl ether than when used with methanol. For example, after the operation for 1.5 h of a catalyst based on H-ZSM-5 zeolite (SiO_2/Al_2O_3 = 55) mixed with SiO_2 (1:1), the conversion of dimethyl ether into hydrocarbons decreased by 30%.[189] Simultaneously, the reaction products showed a marked increase in the concentration of ethylene and propylene, and a decrease in the concentration of C_3 and C_4 alkanes. The low stability of the catalyst in these experiments[189] was apparently partly due to the extensive dilution of the pentasil by silicon dioxide. On H-ZSM-5 zeolite in the pure form, the conversion of dimethyl ether at 350° decreased by only ~10% in the first 9 h, and after use for 100 h it decreased by ~40%.[197]

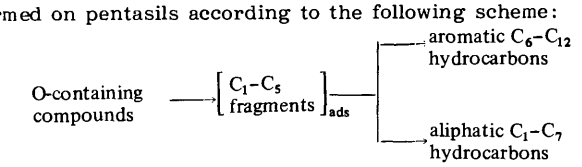
Comparison with first-generation zeolites showed that the conversion of the ether on HY after 9 h decreases by 92%, and erionite and mordenite in the H-forms are almost completely deactivated after use for 6–7 h under the same conditions.

The deactivation of all the zeolites is due to the formation of coke, the quantity of which in the H-ZSM-5 zeolite amounted to only ~2.5 mass % after 9 h, whereas in other zeolites it amounted to ~7–9 mass %.[197] After 100 h, the concentration of coke in the H-ZSM-5 zeolite increased to ~7%. It is suggested that during use, coke formation in the pentasil takes place chiefly on its outer surface, since the small diameter of the zeolite pores prevents bimolecular reactions in them between large molecules, leading to coke precursors (see section II). The coke deposited on the outer surface has little influence on the pentasil activity, which is apparently suppressed by oligomers (or polymers) of ethylene and propylene, which accumulate in the pores on prolonged catalyst use.

The method of preparation of the pentasil has a slight influence on the nature of the transformations of dimethyl ether. Thus ether is converted to a greater extent into ethylene on H-ZSM-5 specimens synthesised in the presence of tetrapropylammonium cations than on specimens obtained using 1,2-diaminohexane[198].

The rate of formation and composition of the products of the transformations of dimethyl ether on H-ZSM-5 pentasil are practically independent of the size of the zeolite crystals and the concentration of Al in them, but change significantly with change in the diameter of the zeolite catalyst pellets[107]. From this and the results of a study of the kinetics of the diffusion and transformations of dimethyl ether on these zeolites, it was concluded[199] that in catalyst pellets with a diameter >2 mm, the rate of the reaction and its selectivity are limited by the diffusion of the molecules in the secondary porous structure. For a smaller pellet diameter, diffusion between the crystallites plays almost no part[107,199]. It was also shown[199] that diffusion in the pores of the pentasil also have very little influence on the rate and selectivity of the transformations of dimethyl ether.

In addition to dimethyl ether, the transformations of diethyl, di-isopropyl, and dibutyl ethers on pentasils have been studied[159]. Since there are no significant differences in the compositions of the products formed from these ethers and also from dimethyl ether, methanol, and acetone, it was concluded that all oxygen-containing compounds are transformed on pentasils according to the following scheme:



Other oxygen-containing compounds. In contrast to alcohols and simple ethers, there have been almost no published studies of the transformations of oxygen-containing compounds of other types (ketones, aldehydes, acids, etc.) on zeolites of the pentasil family. For example, the transformations of acetone have been described only in Refs.152 and 159. Of the total quantity of hydrocarbons formed at 250°, ~60% corresponds to mesitylene, apparently formed on the outer surface of the zeolite by the condensation of three acetone molecules[152]. In addition, the products contain ~19% isobutene and ~19% C_6 and higher aliphatic hydrocarbons. The oxygen-containing products consist chiefly of mesityl oxide (~27%)—the product of the condensation of two acetone molecules—and also C_4 alcohols. At 320°, the total conversion of acetone increases to only ~25%, but the composition of the products changes significantly: among the hydrocarbons, the chief product is isobutene (~83%), and the concentration of mesitylene is only ~2.5%. Approximately 10% of the acetone reacting is converted into CO and CO_2. Increase in temperature to ~400° leads to the almost complete conversion of acetone into C_1–C_{10} hydrocarbons, among which the chief components are xylenes (~22%), C_9 alkylbenzenes (~20%), toluene (13%), a mixture of propylene and propane (~10%), and C_{6+} alkanes and alkenes (~8%).

Table 5. Composition (mass %) of the products of the transformations of aldehydes, esters, and acetic acid on H-ZSM-5 zeolite (371°, 100% conversion).[152]

Products	Original compound				
	CH_3CHO	CH_3CH_2CHO	$n\text{-}C_3H_7\text{—}OOCCH_3$	$n\text{-}C_4H_9\text{—}OOCCH_3$	CH_3COOH
Methane	1.5	0.8	0.1	0.1	0.4
Ethane	0.7	0.4	0.1	0.4	0.1
Ethylene	0.3	0.4	2.7	0.2	0.4
Propane	16.4	7.3	2.1	19.4	0.9
Propylene	0.9	0.6	32.1	0.9	3.3
Isobutane	15.1	4.6	1.0	19.3	1.0
n-Butane	5.8	3.0	0.6	9.2	0.6
Butenes	0.9	0.3	6.9	0.6	71.5[2]
Isopentane	5.8	1.8	0.3	7.9	0.1
n-Pentane	1.0	0.6	0.5	1.9	—
Pentenes	0.2	0.2	2.0	0.1	0.4
C_{6+} aliphatic hydrocarbons	3.2	1.3	3.3	4.8	—
Benzene	1.1	4.1	0.8	2.1	0.1
Toluene	7.9	23,7	6.1	10.9	2.0
Xylenes	20.5	26.4	16.7	11.6	5.1
Ethylbenzene	0.7	2.6	1.4	1.1	0.5
C_9 alkylaromatic hydrocarbons	12.4	18.6	15.2	6.2	11.4
C_{10+} alkylaromatic hydrocarbons	5.6	4.3	8.1	3.3	13.6

[1]Conversion 29.9%.
[2]Including 66.5 mass % isobutene.

Published data[152] on the composition of the products of the transformations of various other oxygen-containing compounds on H-ZSM-5 zeolite are summarised in Table 5. All the compounds studied (except acetic acid) are readily transformed into mixtures of hydrocarbons, whose composition depends on the nature of the starting material. Thus propionaldehyde gives products whose composition is extremely close to the products of the transformations of alcohols (see Table 4). Acetaldehyde and n-butyl acetate, in addition to hydrocarbons, give appreciable quantities of CO and CO_2. The transformation of these compounds into

aromatic hydrocarbons is more selective than the transformation of alcohols. The products of the transformation of n-propyl acetate, in addition to a large quantity of aromatic hydrocarbons (~50%), contain more than 30% propylene.

The most stable compound under these conditions is acetic acid, whose conversion amounts to less than 30%, and only ~58% of the quantity of acid reacting is converted into hydrocarbons. The latter consist chiefly of butenes (66.5% isobutene + 5% butenes) and C_9 and C_{10} alkylaromatic hydrocarbons (~25%).

Thus zeolites of the pentasil family are effective catalysts for the transformations of methanol, dimethyl ether, and other oxygen-containing compounds to give mixtures of C_1–C_{10} hydrocarbons with approximately identical compositions; most of the work in this field has been devoted to the transfromations of methanol. The importance of these studies is not limited to the accumulation of data which can be used to develop the important practical process of motor fuel production. They have developed to a considerable extent the study of the structure and physicochemical properties of zeolites of the new generation and have made a significant contribution to the development of ideas about the catalytic activity of zeolites. They have also initiated studies of the possible application of pentasils in other catalytic processes, in particular the transformations of various hydrocarbons.

IV. TRANSFORMATIONS OF HYDROCARBONS ON PENTASILS

The ability of first-generation zeolites (faujasites, mordenite) to catalyse the transformations of various hydrocarbons was established by a large number of studies, reviewed earlier[40,130]. Thanks to this property, these zeolites have found extensive application as catalysts of a number of processes in petroleum refining and petroleum chemistry. The reactions of hydrocarbons carried out on first-generation zeolites include, for example, cracking, isomerisation, oligomerisation, disproportionation, etc. These and various other reactions of hydrocarbons also take place on zeolites of the pentasil family.

1. Transformations of Alkenes

The possibility of using pentasils to catalyse the transformation of individual C_2–C_5 alkenes and their mixtures into aliphatic and aromatic hydrocarbons with higher molecular weights was shown in the first Mobil Oil patents in 1973–74. In the scientific literature, the first reports of the study of these reactions appeared only in 1979.[87,128,200] In the last two or three years, the number of papers on this topic has increased considerably, and most have been devoted to the study of the transformations of ethylene and other lower alkenes on pentasils.

Transformations of ethylene. The large number of studies of the transformations of ethylene on pentasils[87,103,107,122,125,128,159,161,166,184,186,189,200–205] differ considerably in the reaction conditions and in the types and compositions of the catalysts used. There is therefore often lack of agreement between the data obtained by different authors. For example, in Ref.87 it is reported that on H-ZSM-5 zeolite (SiO_2/Al_2O_3 = 59; 0.38 mass % Na) at 400° and a rate of supply of hydrocarbons of 1.2×10^{-2} mole h^{-1}, ethylene usually shows a low reactivity, but sometimes its conversion reached high values. A low degree of conversion of ethylene on zeolites of the same type was also observed by other workers[122,158,161]. At the same time it is reported that under selected (usually milder) conditions, the conversion of ethylene exceeds 90%.[125,159,189,200–202,204] The available data show that the extent of the conversion of ethylene depends on the rate of supply of the alkene, the temperature of the reaction, and the presence of modifying additives in the zeolite. The influence of these factors on the degree of transformation of ethylene and the composition of the reaction products has not been studied in detail, however.

Experiments with ethylene on different TsVK zeolites with approximately equal SiO_2/Al_2O_3 ratios (~80–82) [200] showed that decrease in the quantity of Na_2O in the zeolite from 1.2 mass % to 0.6 mass % not only increases the conversion of the alkene (from 72% to 98%) but also changes significantly the composition of the reaction products: the gases show a decrease in the concentrations of C_3 and C_4 hydrocarbons by factors of 2 and 5 respectively, and the liquid catalysate, whose yield remains almost unchanged, is enriched in aromatic hydrocarbons, with the simultaneous disappearance of C_4–C_6 alkanes and alkenes. Approximately the same influence on the composition of the gaseous and liquid reaction products is shown by an increase in temperature from 350° to 530°. A significant increase in the concentration of benzene and toluene in the catalysate was observed, however.

The activity, stability, and selectivity of pentasils in the transformations of ethylene depend to a significant extent on the SiO_2/Al_2O_3 ratio[205]. For ultrasil zeolites, at values of this ratio in the range 26–80, the conversion of ethylene at 350° is ~97%, and remains practically unchanged during the experiment. At SiO_2/Al_2O_3 = 190, however, the degree of transformation of C_2H_4, which at the start of the experiment is ~53%, decreases to ~18% in 80 min. Moreover, with increase in this ratio from 29 to 190, the concentration of alkanes in the reaction products decreases considerably. It was therefore suggested[205] that the reactions involving the redistribution of hydrogen take place on the strong acidic centres produced in the pentasils with decrease in the concentration of Al and the total quantity of acidic centres. As already noted in section II, however, no anomalously strong acidic centres have been detected in pentasils. With decrease in the Al concentration, the total number of active centres in the zeolite apparently decreases, and below a certain limit it becomes insufficient for the competing reactions to take place simultaneously on them. The secondary processes, including, for example, the reactions involving the redistribution of hydrogen, should evidently be suppressed to a greater extent.

A comparative study of the transformations of ethylene on H-ZSM-5 and HNaY zeolites by infrared spectroscopy and mass spectrometry also showed[128] that unsaturated hydrocarbons predominate in the products of the reaction on pentasil. Depending on the temperature, the products on this zeolite are either aliphatic C_3–C_7 hydrocarbons (at 100 to 200°) or C_5–C_7 cyclanes and cyclenes (at 200–300°), or C_6 to C_{10} aromatic hydrocarbons (at 320–430°), and the pentasil had a much higher aromatising power than HNaY zeolite. In Refs.204 and 205, no mention was made of the formation of aromatic hydrocarbons in the transformations of ethylene on pentasil.

In the discussion of the products of the transformations of ethylene on pentasils, it should be noted that according to infrared spectroscopy, thermogravimetric analysis, and ^{13}C NMR spectroscopy, ethylene even at 20° is adsorbed on the Brönsted acidic centres of these zeolites and is activated and oligomerised to give long unbranched molecules[103,189,202,203]. It is suggested[103,184] that the oligomerisation of ethylene takes place by a carbenium-ion mechanism, and also that

above 300° the ethylene oligomers may undergo cracking and dehydrocyclisation.

In attempts[103,122,128,189] to model the conditions of the transformation of methanol (and dimethyl ether) into hydrocarbons, the decomposition of ethylene on pentasils in the presence of water was studied. The study of the combined sorption of ethylene and water on H-ZSM-5 zeolite[103] showed that at 20°, the strong Brönsted centres of this zeolite adsorb water preferentially, suppressing the activation and oligomerisation of the alkene. Above 250°, some of the centres become accessible for the adsorption of ethylene, which undergoes transformations to give chiefly alkenes with higher molecular weight, and also aromatic hydrocarbons. The poisoning by water of the acidic centres of H-ZSM-5 zeolite, responsible for the oligomerisation and aromatisation of ethylene, was also observed at a higher temperature (370°).[122] At the same time, water increased the stability of the zeolite and the degree of conversion of ethylene, facilitating cracking reactions. In spite of the suppression by water of the aromatisation of ethylene, the formation of the products of this reaction was observed at lower temperatures in the presence of water than in experiments with the dry alkene. It was suggested[122] that water facilitates the desorption of aromatic hydrocarbons from the zeolite channels by lowering their boiling point, as in steam distillation. The ability of water to increase the rate of desorption of the reaction products was confirmed in a study of the thermal decomposition of ethylene oligomers formed on H-ZSM-5 zeolite[198]. At the same time it was shown that water apparently acts as an additional source of protons, since in its presence there is an increase in the proportion of alkanes in the reaction products.

A fairly complete picture of the influence of water on the transformations of ethylene on ZSM-5 zeolites and on the composition of the products of this reaction is given in a paper[189] which mainly confirms data obtained by other workers[122,198]. According to Ref.189, however, water not only does not decrease the selectivity of the formation of aromatic hydrocarbons from ethylene, but increases it significantly, although this effect becomes slightly weaker on prolonged zeolite use.

Transformations of C_3 and C_4 alkenes. These alkenes are more reactive than ethylene in transformations on pentasils. On three specimens of H-ZSM-5 zeolites at 285–310°, propylene was transformed much more rapidly than ethylene[107].

In a study of the transformations of propylene on ZSM-5 zeolites and silicalite (SiO_2/Al_2O_3 = 59 and 1125 respectively) at 400°, the conversion of the alkene reached 85–94%. The reaction products contained aliphatic and aromatic hydrocarbons with a predominance of C_4 (~40%) and C_6 (~25%) alkanes and alkenes, and also xylenes (~30%).[87] With decrease in temperature to 370°, the conversion of propylene decreased to ~55%, and the reaction products contained ~30% butenes and only ~3% aromatic hydrocarbons[122,167]. Approximately the same results were obtained for but-1-ene.[167] In the transformations of propylene on H-ZSM-5 at 285° and 310°,[107] the predominant formation of C_4 and C_6 aliphatic hydrocarbons and the almost complete absence of aromatisation products were observed.

The transformations of C_3 and C_4 alkenes on TsVK zeolites have been studied in detail[84,88,121,125,206,207]. On the Na-form of this zeolite, propylene at 230–240° and isobutene at 140 to 150° gave liquid products containing C_6–C_9 alkanes and alkenes with normal and *cis*-structures. The yield of these products increased sharply with temperature, reached a maximum (>80%) at 310–320°, and then gradually decreased (broken lines in Figs.7*a* and 7*b*). An increase in the yield of gaseous products, consisting of C_2–C_5 alkanes and alkenes and small quantities of methane (not more than 5–7% at 580°) was observed. Above 320°, the liquid catalysates from both alkenes contained aromatic hydrocarbons (mainly benzene, toluene, and xylenes), whose concentration gradually increased with temperature to 91–93% at 550–580°.

Similar results were obtained on a more active decationated TsVK zeolite (<0.1% Na_2O).[88,207] Comparison with the data for Na-TsVK shows that on H-TsVK (continuous lines in Figs.7*a* and 7*b*), the formation of liquid products begins at lower temperatures; at 320° the catalysates contain not only aliphatic but also aromatic (~15–20%) hydrocarbons, and beginning at 450°, both the yield of liquid catalysate and the concentration of aromatisation products in it remain practically constant (up to 580°). The differences between the Na- and H-forms of TsVK are revealed most clearly under the conditions of the transformations of isobutene (Fig.7*b*), which are characterised by distinct temperature ranges corresponding to different reactions: up to 200°, only dimerisation and trimerisation of isobutene take place; at 200–300°, isomerisation of the resulting oligomers is also observed; and above 300°, aromatisation of aliphatic hydrocarbons begins, and this process predominates at 450–550°. These processes are accompanied by reactions involving

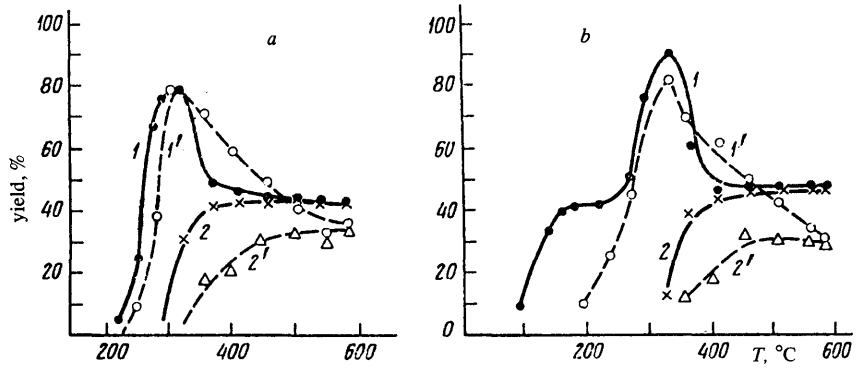


Figure 7. Temperature dependence of the yield of liquid catalysates (*1*, *1'*) and aromatic hydrocarbons (*2*, *2'*) from propylene (*a*) and isobutene (*b*) on the Na-form (broken line) and the H-form (continuous line) of TsVK zeolite[88].

the redistribution of hydrogen, cracking, and interconversion of aromatic hydrocarbons. For propylene, a distinct range corresponding to only oligomerisation was not observed, since significant quantities of the liquid catalysate appeared only at temperatures above 200°, that is under conditions in which intensive isomerisation took place. The small quantities of liquid products formed below 200°, however, contained isomeric hexenes, that is dimers of propylene.

The influence of temperature on the yield and composition of the gaseous products of the transformations of isobutene on H-TsVK zeolite[88] is shown in Fig.8.

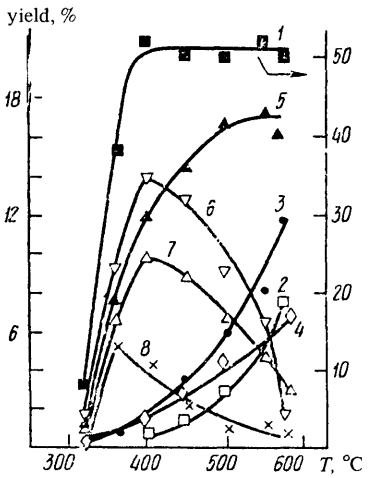


Figure 8. Temperature dependence of the yield of gaseous hydrocarbons from isobutene on H-TsVK zeolite: *1*) total yield of gaseous products, *2*) methane, *3*) ethane + ethylene, *4*) propylene, *5*) propane, *6*) isobutane, *7*) n-butane, *8*) C_5 hydrocarbons.[88]

Comparison with first-generation zeolites (types A, X, Y, and mordenite) [121] showed that the original and decationated forms of TsVK zeolites are much more active in the aromatisation of lower alkenes (450–550°). Neither change in the reaction conditions nor modification of the zeolites by decationation, cation exchange, or the introduction of additives, in the case of first-generation zeolites, led to the production of the high yields of aromatic hydrocarbons reached on pentasil. In addition to high activity in aromatisation, TsVK zeolites were stable and retained their activity for 6–9 h, since coke formation was slight. In contrast to this, first-generation zeolites and catalysts based on them were almost completely deactivated in the first 1–1.5 h of use, as a result of the deposition of coke, the quantity of which reached 10–20%, calculated for the propylene passed. On the TsVK pentasil, the quantity of coke deposited was ~10 times smaller, because of the characteristic features of its porous structure.

A study of the transformations of C_3 and C_4 alkenes on TsVK pentasil containing different quantities of Na and activated at different temperatures (T_{act}) revealed the relationship between the catalytic properties of the pentasil, its composition, and the activation conditions[84]. Increase in the concentration of Na_2O in the zeolite from 0.1 mass % to 1.1 mass % decreased slightly the conversion of the alkene and the yield of liquid catalysate, and also suppressed the aromatisation considerably. The lowest activity was shown by the zeolite specimen containing 1.3 mass % Na_2O, and also 0.25 mass % iron oxide impurity. The complete removal of this impurity and almost all the sodium by decationation gave the most active catalyst specimen, which brought about the greatest conversion of the original alkene and the highest yields of liquid catalysate and aromatic hydrocarbons[84].

Activation at 900–1000° had the greatest influence on the catalytic properties of TsVK zeolite[84]. This thermal treatment led to a decrease in the yield of liquid catalysate and the overall yield of aromatic hydrocarbons from isobutene at 320° and 500°, but at the same time the selectivity of *p*-xylene formation increased considerably. Moreover, with increase in T_{act} from 500 to 1000°, the gaseous reaction products showed a decrease in the concentration of alkanes and an increase in the concentration of alkenes (Fig.9), indicating a decrease in the activity of the zeolite in hydrogen redistribution reactions. These reactions apparently take place on Brönsted acidic centres, the quantity of which decreases on high-temperature treatment as a result of dehydroxylation of the surface (see section II). These data provide another example of the existence of a relationship between the intensity of hydrogen redistribution reactions and the quantity of Brönsted acidic centres in the pentasils, also observed in the transformations of ethylene on ultrasil zeolites[205].

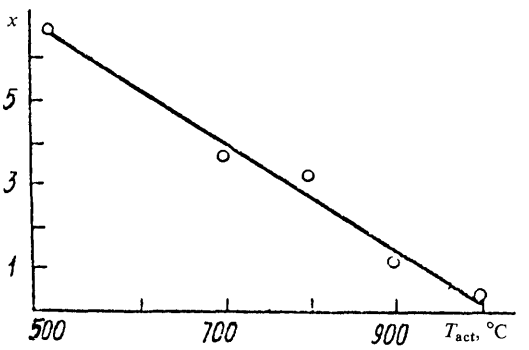


Figure 9. Influence of T_{act} on the ratio of the concentrations (x) of C_2–C_4 alkanes and alkenes in the products of the transformations of isobutene (500 °C) on TsVK zeolite[84].

The addition of vanadium (2.8 mass %) to the Na-form of TsVK zeolite (SiO_2/Al_2O_3 = 70.5, 0.7 mass % Na_2O) decreased considerably the conversion of C_3 and C_4 alkenes (and ethylene), the yield of liquid catalysate, and the total yield of aromatic hydrocarbons[125]. For the more active H-form of this zeolite, the influence of the additive depends on its concentration and on the reaction temperature[208]. The addition of 0.3 mass % vanadium to H-TsVK not only did not decrease, but even increased by a factor of ~1.5, the total yield of aromatic hydrocarbons from isobutene at 320°. Approximately the same effect was observed at 500°, but in this case it was reached at a vanadium concentration of 0.9 mass %. At both temperatures, the conversion of the original alkene remained at 100% throughout the entire range of vanadium concentrations studied (0.3–10.3 mass %).

It was also found[125,208] that the modification of TsVK zeolites by vanadium increases sharply the selectivity of the formation of *p*-xylene (and *p*-ethyltoluene) from lower alkenes, estimated from the ratio of the concentrations of *p*- and *m*-xylenes ([PX]/[MX]) in the reaction products. For the non-modified zeolite[209], the ratio [PX]/[MX] did not exceed 0.44, corresponding to the concentration of these isomers in the equilibrium mixture. In the presence of vanadium, however, this ratio increases by a factor of not less than ~19. For the decationated zeolite, the addition of V led to a slightly smaller increase in the selectivity of the formation of the *p*-isomers of dialkylbenzenes, and this effect increased with increase in the concentration of the additive and with decrease in the reaction temperature (Fig. 10).[208] The results were attributed[125,208] to the influence of the added vanadium on the molecular-sieve and diffusion properties of the TsVK zeolites (see section II). The reasons for the selective formation of the *p*-isomers of dialkylbenzenes will be discussed later, since this phenomenon was observed not only in the transformations of lower alkenes but also in other reactions.

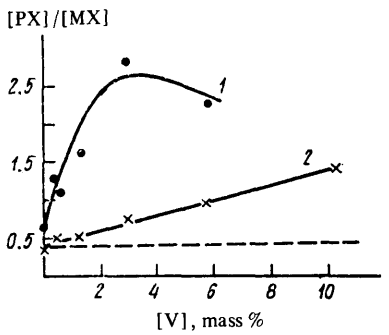


Figure 10. Dependence of the selectivity of formation of *p*-xylene ([PX]/[MX]) from isobutene on the vanadium concentration in H-TsVK zeolite at 320 °C (*1*) and 500 °C (*2*); the broken line gives the ratio at equilibrium[207].

Apart from these studies, only a comparative kinetic study of the isomerisation of but-1-ene and *cis*-but-2-ene on H-ZSM-5 and H-Fu-1 zeolites (SiO_2/Al_2O_3 = 60 and 22 respectively), and also on an amorphous aluminosilicate, at 0° in a static system, has been carried out[210]. The results indicated that the isomerisation of butenes on these catalysts takes place by a carbenium-ion mechanism on the Brönsted acidic centres, which are much more stable in H-ZSM-5 than in H-Fu-1 or in the amorphous aluminosilicate.

The transformations of alkenes with higher molecular weights on pentasils have been described in only a few papers. The transformations of oct-1-ene on the Na-form of TsVK zeolite at 175–550° have been studied in most detail[212]. Only the reaction involving the movement of the double bond in octene took place intensively below 250° on this zeolite. At 250 to 300°, structural isomerisation of the octene began, and the yield of linear isomers decreased to 10%. Under these conditions, appreciable cracking of oct-1-ene and its isomers was observed, leading to a decrease (to ~75%) in the yield of liquid catalysate, in which aliphatic C_6 and C_7 hydrocarbons appeared. At 400°, oct-1-ene gave appreciable quantities of aromatic hydrocarbons, the concentration of which in the catalysate increased sharply with increase in temperature and when the zeolite was modified by added V, Pt, and Rh.[212] Thus as with lower alkenes, the introduction of added vanadium increased to a considerable extent the selectivity of the formation of the *p*-isomers of xylene and ethyltoluene from oct-1-ene, but this selectivity decreased with increase in temperature. These effects were not observed on the catalysts prepared by modifying the pentasil by added Pt and Rh.

The studies have included not only oct-1-ene but also the transformations of 3,3-dimethylbut-1-ene, which on H-ZSM-5 zeolite at 370° readily underwent isomerisation to 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene, and also cracking to give appreciable quantities of propane and butane. The reaction products contained a small quantity of C_6–C_9 aromatic hydrocarbons[161].

Thanks to the molecular-sieve properties of ZSM-5 zeolite, the rate of the isomerisation of C_6–C_8 alkenes on this catalyst (150–175°) decreases with increase in the degree of branching of the molecule (hex-1-ene > 6-methylhept-1-ene ≫ 3-ethylpent-1-ene ≫ 4,4-dimethylhex-1-ene).[113] The selective hydrogenation (at 275°) of hex-1-ene in its mixtures with 4,4-dimethylhex-1-ene on a Pt-ZSM-5 ion-exchange zeolite catalyst is also possible[113].

The transformations of cycloalkenes on pentasils has not been specially studied. Infrared spectroscopy has shown[212], however, that even at 40–45°, cyclopentene, cyclopentadiene, and cyclohexene are strongly adsorbed on HZ-79 zeolite (an analogue of ZSM-5 zeolite) with the formation of the same oligomers as with the linear alkenes. Partial transformation of the cycloalkenes into aromatic hydrocarbons was observed. With increase in temperature to 200–360°, the infrared spectra of the adsorbed cyclenes show an increase in the strength of the bands corresponding to the formation of aromatic structures. The mechanism of formation of linear oligomers and aromatic hydrocarbons from cycloalkenes has not yet been determined.

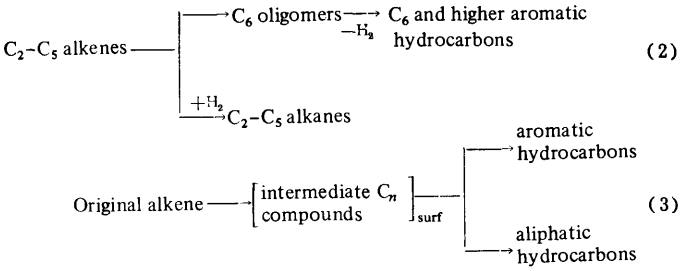
2. Mechanism of the Transformations of Alkenes on Pentasils

As already noted in section II, the nature of the catalytic activity of zeolites of the pentasil family and first-generation zeolites is the same and is determined by the presence of surface OH groups, which act as Brönsted acidic centres. Thus the mechanism of the transformations of alkenes on pentasils apparently corresponds to present-day ideas, according to which these reactions on zeolites involve the formation of carbenium ions as a result of the protonation of the reacting molecules on the acidic OH groups[130]. There are very few published papers, however, specially devoted to the study and examination of the mechanism of the transformations of alkenes on pentasils. In most cases, this question is discussed in direct relation to the mechanism of formation of hydrocarbons from methanol and dimethyl ether (see section III), which assumes the participation of molecules of oxygen-containing surface compounds either in the growth of the hydrocarbon chains or in the regeneration of the Brönsted acidic centres.

The transformations of lower alkenes in mixtures of various hydrocarbons in the absence of oxygen-containing compounds is usually represented by the general schemes (1),[186] (2),[184] and (3):[87,159,20]

$$C_nH_{2n} + HOZ \rightleftarrows [C_nH_{2n+1}OZ \leftrightarrow C_n^+H_{2n+1}\,\bar{O}Z] \rightarrow C_mH_{2m} + HOZ \quad (1)$$

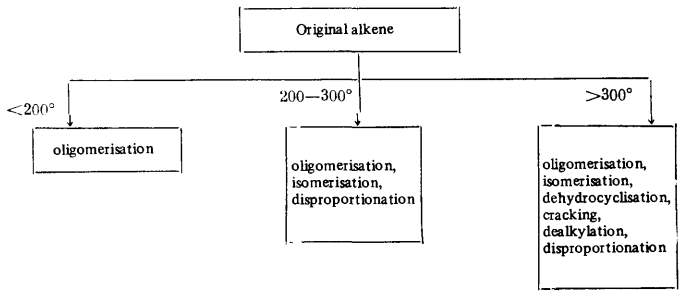
Z = zeolite, $m \gg n$



In Eqn.(3), the intermediate compounds are either "unsaturated residues" of the original molecules[87] or C_1–C_4 fragments of these molecules, adsorbed on the zeolite surface[159, 200].

From the composition of the products formed from lower alkenes on TsVK pentasils of different temperatures, a sequence of transformations of the original hydrocarbons and the products formed from them was proposed[88,207] (scheme 1).

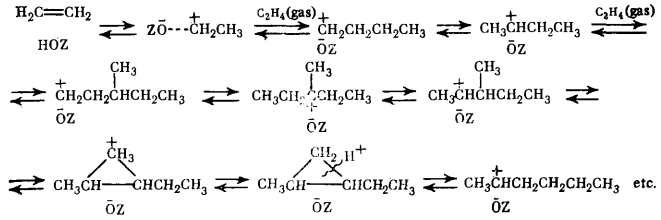
Scheme 1



Although this scheme says nothing about the mechanism of the transformations of the alkenes, all the reactions in it can take place on the acidic centres of zeolite catalysts by a carbenium-ion mechanism[130]. Moreover, this scheme shows good agreement with the conclusion that there are three temperature ranges of transformations of C_2–C_4 alkenes on ZSM-5 zeolites, reached on the basis of thermogravimetric analysis and high-resolution ^{13}C NMR spectroscopy[189,201,202]. According to these data, the alkenes below ~30° readily undergo oligomerisation to give long unbranched molecules, and the rate of this reaction for ethylene is lower than that for other alkenes. These oligomers are formed and strongly adsorbed inside the pores of the zeolites, filling them completely. With increase in temperature, the rate of oligomerisation, calculated for one active centre, increases for all the alkenes. At ~130°, slight cracking of the oligomers is observed, and above 230° the rate of cracking begins to exceed the rate of oligomerisation. Thus above 230 °C, blocking of the pores of the zeolite by oligomers does not take place, and the reacting molecules diffuse freely through the channels of the pentasil, which at these temperatures is an active catalyst for the transformations of lower alkenes. An infrared spectroscopic study of the sorption of alkenes on HZ-79 zeolite indicated that the alkene oligomers formed apparently act as the source of aromatic hydrocarbons[197], whereas on HNaY zeolite they are mainly transformed into coke[212].

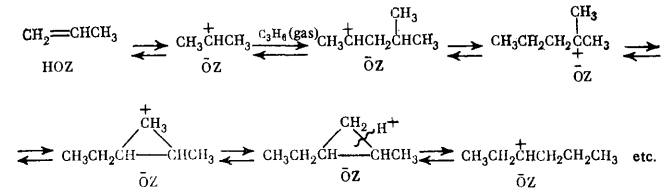
The mechanism of the oligomerisation of ethylene with the formation of hydrocarbon chains containing an average of 25 carbon atoms is represented by scheme 2 [201,202] involving carbenium ions formed on the Brönsted acidic centres of the pentasil:

Scheme 2



The last stages of this scheme explain the formation of linear molecules from propylene and other alkenes, whose oligomerisation should give only branched molecules (scheme 3).

Scheme 3



The oligomers formed from propylene and isobutene contain an average of 6–8 carbon atoms. The differences in the rates of the oligomerisation of ethylene and the C_3 and C_4 alkenes were attributed to a difference in the stability of the primary, secondary, and tertiary carbenium ions formed from these alkenes[201,202].

Similar schemes have been used to represent the transformations of alkenes with higher molecular weights (3,3-dimethylbut-1-ene), including not only oligomerisation but also other reactions such as the aromatisation of lower alkenes[161].

These ideas on the mechanism of the reactions of alkenes on pentasils, together with data on the specific molecular-sieve properties of these zeolites, have made it possible to explain the predominance of certain hydrocarbons and the absence of others in the products of the transformations of alkenes[184].

Thus the mechanism of formation of carbenium ions on Brönsted acidic centres has been successfully applied to the transformations of alkenes on zeolites of the pentasil family. At the same time there are a number of unsolved problems, related to the nature of the catalytic action of these zeolites, which can be solved only by further studies.

3. Transformations of Saturated Hydrocarbons

The ability of zeolites of the pentasil family readily to adsorb and bring about the selective cracking of alkanes with the normal structure has made these zeolites promising catalysts for processing high-alkane petroleums and petroleum products[8,16,17,213]. It will be shown below that pentasils can apparently catalyse not only cracking but also other transformations of saturated hydrocarbons of practical importance. The reactions of alkanes on pentasils have been insufficiently studied, however.

Transformations of alkanes. Recently published data[214] on the possibility of transforming methane and ethane into C_6–C_{10} aromatic hydrocarbons on TsVM zeolites are of considerable interest. In a pulse reactor on this zeolite ($SiO_2/.Al_2O_3$ = 33.3), containing added group VIII metals (0.2 to 1.0%), methane at 600° in the absence of oxidising agents gives benzene in >6% yield, calculated on the hydrocarbon passed. The yield of aromatic hydrocarbons from ethane on the non-modified zeolite was ~10%, and on the zeolite containing added metal the yield reached 20%, but the reaction was less selective.

The formation of benzene, toluene, xylenes, and trimethylbenzenes from methane has also been observed under the conditions of its oxidative dehydrogenation on pentasils modified by added transition metal compounds[215]. In this case the selectivity of the reaction corresponds to 10–20% of the transformed methane.

Pentasils can bring about the aromatisation of alkanes with higher molecular weights—hexane, 3-methylpentane, 2,2-dimethylbutane, and iso-octane[87,159,216]. The liquid catalysates formed from n-hexane, 3-methylpentane, and iso-octane on TsVK zeolite (flow reactor, 450°), in addition to the non-transformed alkane and cracking products, contained 50, 42, and 10% aromatic hydrocarbons respectively. Similar results were obtained on the same zeolite under pulse conditions, and also in a flow system on H-ZSM-5 zeolite at 400°.[87] According to these data[87], the conversion of the hexane isomers decreased with increase in the kinetic diameter of their molecules. Together with the results of sorption measurements, these data indicated that the rate of the transformations of the alkanes is limited by the rate of their diffusion into the zeolite pores. Thus n-hexane penetrates rapidly into the pores and is readily transformed on the active centres localised in them. 2,2-Dimethylbutane, however, must apparently first undergo isomerisation on the outer surface to give isomers which can more readily diffuse into the zeolite channels, where they undergo further transformations. These suggestions were confirmed in experiments using 4-methylquinoline and ammonia, introduced into the reactor together with the hydrocarbons. The addition of 4-methylquinoline, which can be adsorbed only on the outer surface of the zeolite, had practically no influence on the conversion of n-hexane, but suppressed almost completely the transformations of 2,2-dimethylbutane. The addition of ammonia, which readily penetrates into the pores, deactivated the catalyst for the transformations of both hydrocarbons. When the supply of ammonia was stopped, the catalytic activity of the pentasil was gradually restored as desorption took place.

The acidic properties of the pentasils indicate that they may be active in the isomerisation of alkanes. In fact, n-butane, n-pentane, and n-hexane undergo isomerisation on TsVK zeolites (SiO_2/Al_2O_3 = 33.3, 47, and 83) at 250–400° under a pressure of 30 atm.[91] Extensive hydrocracking and disproportionation of these alkanes took place simultaneously. The relative extent to which these last reactions took place decreased sharply when the zeolites were modified with palladium. The greatest activity and selectivity in the isomerisation of n-pentane was shown by the 0.5% Pd/TsVK catalyst prepared by ion exchange, on which the yield of isopentane at 330° reached ~60 mass %, and the yield of the products of hydrocracking and disproportionation amounted to only 2.8 mass % and 1.3 mass % respectively[91].

It should be noted that n-decane, which has a higher molecular weight, underwent hydrocracking preferentially on the 0.5% Pt/H-ZSM-5 ion-exchange catalyst, and underwent isomerisation to only a slight extent[90]. The composition of the products of the isomerisation of n-decane, in which 2-methylnonane predominated, differed considerably from the equilibrium composition. The results were attributed[90] to the influence of the molecular-sieve properties of the zeolite, which prevents the formation of highly branched isomers.

The isomerisation of isobutane on H-ZSM-5 zeolite ($SiO_2/.Al_2O_3$ = 100; 0.01 mass % Na; 350°) took place much more intensively than that of n-butane, and the rate of reaction on pentasil was ~70 times slower than that on H-mordenite.[217] Moreover, the pentasil showed almost no activity on the disproportionation of isobutane to propane and pentanes, accompanying the isomerisation. Since the isomerisation and disproportionation of isobutane are bimolecular reactions, the low activity of the pentasil in these reactions was attributed to the difficulty of formation of bulky intermediate compounds in the narrow pores, that is to the molecular-sieve selectivity with respect to the transition state (see below).

The cracking of alkanes on pentasils has been studied in much more detail than isomerisation. H-ZSM-5 zeolite is more active in the cracking of n-hexane than H-mordenite.[217] The activity of both zeolites in this reaction is much greater than that of other zeolites (NaY, LaY, HY, MgX, and Na-ZSM-5), industrial cracking catalyst (ICC), and amorphous aluminosilicate (AAS).[101] The relative activity ($\alpha = k_X/k_{ICC}$, where k_X and k_{ICC} are the rate constants of the cracking on the catalyst being studied and on ICC respectively) for H-ZSM-5 and HM were more than 10^5, whereas for the other catalysts the values of α did not exceed 10^3.[101] The ZSM-5 zeolites showed a high resistance to treatment with steam at a high temperature, and a high stability due to the low degree of coke formation in these catalysts. The products of the cracking of n-hexane on these zeolites at low degrees of conversion of the hydrocarbon (5–20%) contained chiefly propane, n-butane, and isobutane. With increase in the conversion of the original alkane to ~90% at higher temperatures, the formation of aromatic hydrocarbons and an increase in the concentration of ethylene in the reaction products were observed[101].

The cracking of n-octane on TsVK pentasil and zeolites of type Y, mordenite, and erionite can be represented by the following general scheme[134]:

Alkane → "unsaturated fragments" → alkanes and aromatic hydrocarbons → polycyclic hydrocarbons (coke)

The reactions involving the redistribution of hydrogen and secondary transformations of alkenes apparently take place at a lower rate on pentasil than on other zeolites[134]. Moreover, for pentasil the rate of desorption of monocyclic aromatic hydrocarbons is much greater than the rate of their transformation into polycyclic systems, which act as coke precursors. These characteristic features were attributed[134] to the unusual geometry of the pentasil pores and the low density of hypothetical proton-donor centres (see section II), whose existence in zeolites has not yet been proved.

The activity of pentasils of different type (ZSM-5, TsVK, TsVM, ultrasil) in the cracking of alkanes decreases with decrease in the Al concentration in the zeolite framework[89,101,218], with increase in T_{act},[85] and with decrease in the quantity of acidic OH groups on treatment of the zeolite with ammonia[143].

The relative rate of the cracking of alkanes decreases with decrease in the length of the carbon chain of the molecules ($n\text{-}C_7 > n\text{-}C_6 > n\text{-}C_5$) and with increase in the degree of branching of the alkane (n-alkane > 2-methylalkane > 3-methylalkane > dimethylalkane > ethylalkane).[100] The rate of transformation of the different molecules is apparently limited by the rate of their diffusion into the zeolite pores, which is determined by the size and shape of the

molecules; the length of the molecules is slightly less important than the kinetic diameter[100]. A decrease in the reaction rate with increase in the degree of branching of the molecules was also observed in the cracking of n-octane and iso-octane on ZSM-5 pentasils and ultrasil[101,141,143,164]. With increase in temperature, the differences in the rate of cracking of alkanes with different structures on these zeolites decreased considerably[100,143]. It was suggested[100] that in contrast to the first-generation zeolites, pentasils have a "dynamic" molecular-sieve selectivity with respect to the reacting molecules, as a result of which the molecules whose kinetic diameters differ by more than 1 Å can diffuse into the pores of these zeolites at approximately equal rates. Unfortunately, no explanation for the reasons for this phenomenon was given[100].

A number of papers have been devoted to the cracking of individual alkanes or high-alkane petroleum fractions on complex catalysts containing pentasils as one of the components. For example, the cracking of n-hexane has been studied on zeolites of the ultrasil type mixed with 30–90% of a binding agent (Al_2O_3, Al_2O_3–SiO_2, etc.).[219] The high cracking activity of these catalysts was combined with good isomerisation properties. The cracking products contained chiefly C_4 and C_5 hydrocarbons, including the iso-compounds. The addition of 1% Pd to these catalysts increased their isomerisation activity considerably, but decreased significantly the yield of cracking products. Increase in the quantity of binding agent and in the ratio SiO_2/Al_2O_3 in the zeolite had a similar effect.

A number of papers deal with the preparation and study of two-zeolite ("hybrid") cracking catalysts containing TsVM zeolites or ultrasil, and also first-generation zeolites (types X, Y, and Ln-Y).[220–225] The study of the catalytic properties of these systems in the cracking of individual alkanes (n-heptane) and petroleum fractions (gas oil, kerosene–gas oil fraction) showed that the yield of unsaturated hydrocarbons increases considerably in the presence of pentasil.

The possibilities provided by the use of zeolites of the pentasil family as industrial cracking catalysts, and the present state of the production of these zeolites in the Soviet Union have been examined in detail[226].

The transformations of cycloalkanes on zeolites of the pentasil family are described in very few papers. The possibility of obtaining high yields of aromatic hydrocarbons (benzene, toluene, xylenes, and other alkylbenzenes) from cyclopentane, cyclohexane, and methylcyclohexane on TsVK zeolite at 450° under flow and pulse conditions has been reported[159,216]. The same products in approximately the same proportions were formed in all cases, irrespective of the original hydrocarbon. Comparison with corresponding data for ethylene and n-hexane indicated that the reactions of the lower alkenes, alkanes, and cycloalkanes take place according to the same scheme involving the initial splitting of the original hydrocarbon into C_1–C_4 fragments, which are adsorbed on the zeolite surface.

In addition to these data, it has been reported[227] that decalin is transformed to a very slight extent on an experimental industrial cracking catalyst containing 20% H-ZSM-5 zeolite in a kaolin matrix.

4. Reactions of Aromatic Hydrocarbons

The interconversion and alkylation of aromatic hydrocarbons, which are of considerable practical importance, have been studied in detail on first-generation zeolites[130,209]. An important contribution to these studies has been made by Soviet scientists[40]. Pentasils have also been recommended as extremely effective catalysts for these reactions[18–21,228–239].

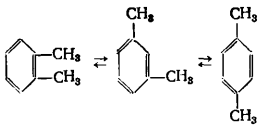
The primary reaction of aromatic hydrocarbons on pentasils is the *selective isomerisation* of *m*- and *o*-xylenes to give the *p*-isomer. In some countries, this process, based on ZSM-5 pentasil, has been carried out on the industrial scale in recent years[38,110].

A number of scientific papers deal with the study of this reaction on pentasils[149,240–245]. For example, the isomerisation of *m*- and *o*-xylenes on the Na- and H-forms of TsVK zeolite, on H-mordenite (HM), and on dealuminated mordenite (DM) was studied in detail[240] to determine the reasons for the high selectivity of the formation of *p*-xylene from different alkenes on pentasils[84,88,125]. The activity of the catalysts studied in this reaction increased in the order Na-TsVK < H-TsVK < HM < DM. With the exception of HM, whose activity decreased by a factor of 2 after 70 min, all the catalysts showed stable operation for 1.5–2 h. The TsVK zeolites catalysed practically only the isomerisation of xylenes, whereas on HM and DM, appreciable disproportionation of xylenes took place to give toluene and trimethylbenzenes (Fig.11). A significant difference was also observed in the ratio of the products of the isomerisation of *m*- and *o*-xylenes on TsVK zeolites and mordenite. For Na- and H-TsVK, the values of the ratio of the concentrations of the isomers formed from *o*-xylene ([PX]/[MX]) were the same, were appreciably greater than the corresponding values for HM and DM, and approached the equilibrium value more rapidly with increase in the degree of conversion (Fig.12*a*). In the isomerisation of *m*-xylene on H-TsVK, the values of the corresponding ratio [PX]/[OX] were greater than the equilibrium value throughout the entire range of degrees of conversion, and with decrease in the conversion from 50% to 15%, this ratio increased from 1.5 to 3.6. In contrast to this, for DM the values of the ratio [PX]/[OX] practically corresponded to the equilibrium value for all degrees of conversion of the original isomer (Fig.12*b*).

Similar results were obtained in experiments with *m*-xylene on H-TsVK and HY zeolites[241]. The data given in Ref.240 were completely confirmed in a comparative study of the transformations of all three xylene isomers on H-ZSM-5, HY, and HM zeolites[242]. The H-ZSM-5 zeolite showed a high activity in the isomerisation of the xylenes, which took place selectively to give the *p*-isomer. This zeolite also showed a very low activity in the disproportionation of dialkylbenzenes, and was completely inactive in the transformations of 1,2,4-trimethylbenzene. All these date made it possible to reach conclusions about the size of the zeolite channels and the cavities formed by the intersection of these channels. It was suggested[242] that the isomerisation of xylene could be used to estimate the porous structure of pentasils instead of the method widely used at present, involving the determination of the "permeability index" (constraint index)[243] $\omega = k_{nh}/k_{2mp}$, where k_{nh} and k_{2mp} are the rate constants for the cracking of n-hexane and 2-methylpentane respectively.

The activity of pentasil in the isomerisation of *m*-xylene and the selectivity of this reaction under pulse conditions are influenced considerably by the composition of the zeolite, its degree of decationation, and the activation conditions, and also by the extent of the poisoning of the acidic centres by ammonia, pyridine, or quinoline[244]. The selective poisoning of the pentasil NiH-ZSM-5 by ammonia suppresses the activity of the acidic centres responsible for dealkylation and disproportionation side reactions, leading to an increase in the selectivity of the isomerisation of *m*-xylene to the *o*- and *p*-isomers.[245]

In contrast to these studies[240-242], other studies[246] reported the selective formation of *p*-xylene from the *m*- and *o*-isomers on H-ZSM-5 zeolite only after its modification by added phosphorus and magnesium. In other respects, the data[246] agreed with the data obtained by other workers. The rates of isomerisation of the xylenes decrease in the order *p*-xylene > *m*-xylene > *o*-xylene in the ratio 5 : 2.5 : 1. Since bimolecular reactions in the channels of the zeolites of the pentasil family are difficult, it was suggested[246] that the isomerisation of xylenes can apparently take place by the intramolecular successive displacement of the methyl group:



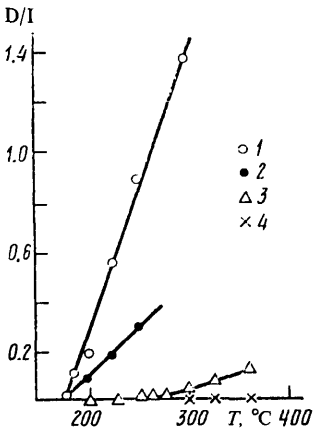
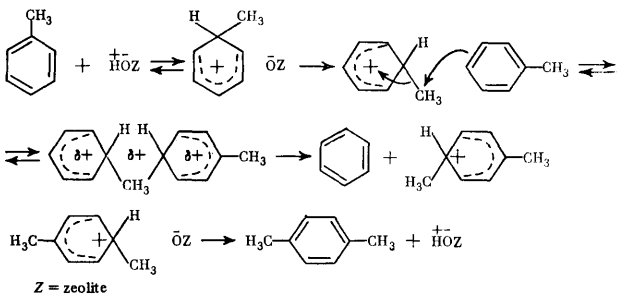


Figure 11. Temperature dependence of the ratio of the concentrations of disproportionation and isomerisation products (D/I) of *o*-xylene for the zeolites DM (*1*), HM (*2*), H-TsVK (*3*), and Na-TsVK (*4*).[242]

In addition to the isomerisation of xylenes, the *disproportionation of toluene* to benzene and xylenes takes place selectively on pentasils. It should be noted that this reaction takes place on pentasils less intensively than isomerisation, and the selective formation of *p*-xylene is observed only when the zeolite is modified by various additives, or when the conversion of toluene is decreased by changing the reaction conditions.

With increase in temperature from 400° to 600° (at a mass rate of supply of toluene of ~3.5 h^{-1}), the conversion of toluene to benzene and xylenes on H-ZSM-5 zeolite increased from 8% to 52%, but the ratio of the xylene isomers in the reaction products remained almost unchanged and practically corresponded to the equilibrium value[109,246,247]. A significant increase in the yield of *p*-xylene was observed only at 550°, when as a result of an increase in the rate of supply of toluene to 30 h^{-1} its conversion decreased from 40% to ~13%. The xylene fraction contained 35, 46, and 19% of the *p*-, *m*-, and *o*-isomers respectively[109,246]. Approximately the same effect was observed on large (~3 μm) crystallites of H-ZSM-5 zeolite at a high rate of supply of toluene. The greatest selectivity of *p*-xylene formation was achieved on zeolite specimens modified by the addition of various elements, in particular magnesium and boron[246,247]. As in the modification of TsVK zeolite by vanadium (see above), however, the introduction of these additives decreased considerably the conversion of the original hydrocarbon. The rate of the disproportionation of toluene on modified H-ZSM-5 zeolite specimens was 10^2 times lower than the rate of isomerisation of xylenes[246]. It was suggested that the mechanism of disproportionation involves the reaction of the toluene molecule with the proton of a Brönsted acidic centre and subsequent transfer of a methyl group (scheme 4).[247]

Scheme 4



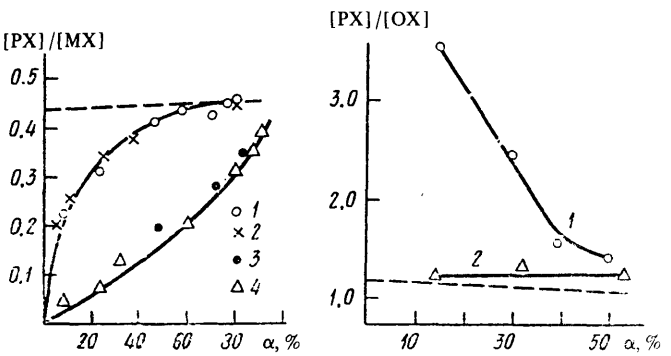


Figure 12. Dependence of the ratio of the concentrations of the products of the isomerisation of *o*-xylene (*a*) and *p*-xylene (*b*) on their conversion (α) on the zeolites H-TsVK (*1*), Na-TsVK (*2*), HM (*3*), and DM (*4*); the broken lines give the ratio at equilibrium[242].

In experiments with toluene (420° and 500°) in the absence of a carrier gas, HY zeolites, HM, omega, and offretite showed a much higher initial activity than H-ZSM-5 zeolite, catalysing both disproportionation and other reactions[248,249]. The pentasil, however, was distinguished by its high stability and ability to bring about the selective conversion of toluene into benzene and a mixture of xylene isomers with the equilibrium composition. An increased concentration of *p*-xylene in this mixture, relative to the equilibrium concentration, was obtained only in experiments with H-ZSM-5 zeolite in which the toluene was diluted with a carrier gas (Ar or H_2), accompanied by a decrease in the conversion of the original hydrocarbon[250]. The greatest yield of *p*-xylene was observed in the presence of H_2, although the side reaction of toluene demethylation simultaneously increased.

Under the conditions of the disproportionation of toluene without a carrier gas (350°), HY zeolites and HM are rapidly deactivated as a result of coke formation, and with increase in their deactivation there is a significant increase in the concentration of *p*-xylene in the reaction products[248]. This was also observed for HY and H-ZSM-5 zeolites when the reaction was carried out in a stream of nitrogen[251]. An increase in the selectivity of *p*-xylene formation was not observed in a stream of H_2.

A study of the disproportionation of toluene on H-ZSM-5 and H-ZSM-11 zeolites showed a slight difference in the behaviour of these pentasils: H-ZSM-11 was slightly less active but more stable than H-ZSM-5, on which *p*-xylene is formed with a greater selectivity than on H-ZSM-11.[251]

The disproportionation of ethylbenzene takes place selectively on HNa-ZSM-5 zeolite, and its total conversion at 200° is 4.4%.[252]

The alkylation of aromatic hydrocarbons, which has been studied in detail on first-generation zeolites[209], is another reaction which takes place on pentasils. Considerable attention has been paid to the study of the reaction of pentasils between toluene and methanol, which may give considerable quantities of *p*-xylene. On different cation-exchange forms of Y zeolite, this reaction gives products containing up to 40–50% *p*-xylene.[253,254] The conversion of methanol on pentasils in this reaction was usually 100%, and the reaction products, in addition to unreacted toluene, contained a mixture of xylene isomers and small quantities of benzene and C_9 and C_{10} alkylbenzenes[109,246,255]. The proportion of aromatic hydrocarbons formed from methanol was very low. Under the mildest conditions (t < 300°, short contact time), the products also contained traces of methanol, dimethyl ether, formaldehyde, CO, and CO_2.[255] The conversion of toluene, the yield of xylenes, and the concentration of the *p*-isomer in them depended on the reaction conditions and the catalyst composition.

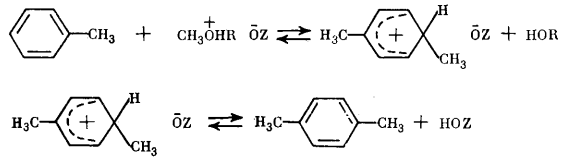
On non-modified H-ZSM-5 and H-ZSM-11 zeolites, this reaction gave a mixture of xylene isomers with a composition close to the equilibrium composition[246,255,256]. The selectivity of *p*-xylene formation on H-ZSM-11 was slightly higher than that on H-ZSM-5. This conclusion requires verification, however, because of the marked differences in the reaction conditions on these zeolites[255].

As in the case of the disproportionation of toluene, a significant increase in the concentration of *p*-xylene in the products of the alkylation on pentasils was observed when large crystals (~3 μm) were used[109,246], and also after an interval from the start of the catalyst operation at high temperatures (550° and 700°).[246,255,256] The selective formation of *p*-xylene in the alkylation of toluene by methanol was also observed not under flow conditions but under pulse conditions[257,258].

A sharp increase in the selectivity of this reaction with respect to *p*-xylene, as in the case of other reactions, was observed when H-ZSM-5 zeolite was modified by various additives[109,246,255,256]. For example, when not less than 16% MgO was introduced by impregnation into H-ZSM-5, the alkylation products showed an increase to ~90% in the concentrations of xylenes, of which more than 90% corresponded to the *p*-isomer. The cation-exchange Mg-H-ZSM-5 zeolite, in which the quantity of Mg was ~13 times lower than that in MgO-H-ZSM-5, at 400° showed approximately the same activity as the non-modified zeolite, but the selectivity of the reaction with respect to *p*-xylene was slightly greater.

The alkylation of toluene by methanol on H-ZSM-5 zeolite with added P, B, Mg, and other elements has been studied in detail at different temperatures, pressures, reagent ratios, and reagent supply rates[246,255]. The greatest effects were obtained on H-ZSM-5 modified using phosphorus (~3–8%), introduced by impregnating the zeolite with solutions of phosphoric acid, diphenylphosphinic acid, methyl phosphite, chlorodiphenylphosphine, or dichlorophenylphosphine. On these catalysts, by varying their composition and the reaction conditions, it was possible to obtain alkylation products containing up to 80–90% xylenes, of which 50–80% corresponded to the *p*-isomer.

In an examination of the possible mechanism of the alkylation of toluene by methanol on pentasils with allowance for the presence of Brönsted acidic centres on these zeolites, it was suggested[186,255] that this reaction takes place according to the following scheme:



R = H, CH_3; Z = zeolite.

According to the rules of electrophilic substitution in aromatic compounds, the chief products of this reaction should be *o*- and *p*-xylenes. The formation of a mixture of all three isomers is due to the isomerisation of the alkylation products formed initially. On non-modified pentasils, the rate of isomerisation of xylenes (w_i) is 10–15 times greater than the rate of alkylation (w_a), whereas on the modified specimens, w_a is 7–15 times smaller than w_i.[246] At the same time, the isomerisation of xylenes takes place preferentially on the strongest Brönsted acidic centres of the pentasils[256]. Thus the selective formation of *p*-xylene in the alkylation of toluene by methanol on pentasils should apparently take place in those cases where these centres are suppressed either by a modifying additive or as a result of treatment with water vapour at high temperature.

In the alkylation of benzene by ethanol on ZSM-5 zeolites (in the pure form or forms modified by phosphorus or boron), the ethyl group is introduced into benzene directly from the alcohol without the intermediate formation of ethylene[186,258].

Like first-generation zeolites, zeolites of the pentasil family are effective catalysts for the alkylation of aromatic hydrocarbons by alkenes. A process was recently developed for obtaining ethylbenzene by the alkylation of benzene by ethylene on ZSM-5 pentasils[238,239]. Pilot-plant and large-scale industrial experimental tests of this process demonstrated a number of advantages of the new catalyst, particularly its high stability and ease of regeneration.

The alkylation of aromatic hydrocarbons by alkenes can take place during any process on pentasils if alkenes and aromatic compounds are present in the system as starting materials or final products. For example, this reaction has been observed[100] under the conditions of the cracking of mixtures of alkanes, accompanied by the formation of a small quantity of benzene and toluene. The ratio of the rates of the alkylation of toluene and benzene by the fragments of molecules undergoing cracking is ~0.7, whereas for the usual heterogeneous or homogeneous systems this ratio is 1.4.

In the alkylation of benzene by ethylene on TsVK zeolites[259], in addition to ethyl and diethylbenzene, the reaction products contained cumene and s-butylbenzene, the yields of which decreased with increase in temperature (Table 6). The formation of these products is evidently due to the

ability of the temperatures to catalyse the oligomerisation of ethylene with the subsequent splitting of the oligomers and disproportionation of the fragments formed. The products of these transformations can then alkylate benzene.

Table 6. The alkylation of benzene by ethylene on ultrasil zeolites ($v = 1.2\ h^{-1}$, molar ratio $C_6H_6 : C_2H_4 = 3:1$).[259]

T, °C	C_2H_4 conversion, %				S, A/B	T, °C	C_2H_4 conversion, %				S, A/B
	to EB (A)	to IPB	to SBB	total (B)			to EB (A)	to IPB	to SBB	total (B)	
	H-TsVK ($x = 60$)						H-TsVK ($x = 172$)				
250	20.2	12.2	6.4	55.0	36.7	250	18.6	9.5	7.3	34.0	54.6
300	53.6	3.5	0.7	80.2	67.0	300	41.7	7.4	1.2	68.4	61.1
350	81.0	1.3	traces	99.0	81.8	350	73.0	1.6	traces	95.0	76.9

Note: EB = ethylbenzene, IPB = isopropylbenzene, SBB = s-butylbenzene, x is the molar ratio SiO_2/Al_2O_3, and S is the selectivity.

The formation of "anomalous" alkylation products was also observed in a study of the reaction of benzene with propylene on ultrasil zeolites[260–262]. These products contained s- and n-butylbenzenes, s- and n-pentylbenzenes, and s- and n-hexylbenzenes. Unlike zeolites of type Y, ultrasil did not give polyalkylbenzenes, and the formation of monoalkylbenzenes with a branched side chain was hindered. The temperature dependence of the composition of the products is complex[260,261], since change in temperature leads to a change in not only the rate of alkylation but also the rate of the transformations of propylene and its oligomers, taking place by a carbenium-ion mechanism. With increase in the degree of decationation of the pentasil there is an increase in its activity and an increase in the selectivity of the reaction with respect to the formation of n-propylbenzene and "anomalous" alkylation products. There is a simultaneous decrease in the stability of the zeolite, probably as a result of the blocking of the active centres by condensation products.

Published information on other reactions of aromatic hydrocarbons on pentasils is limited to data[113] on the selective hydrogenation of styrene in its mixtures with 2-methylstyrene on Pt-ZSM-5 ion-exchange catalyst (400°) and the selective oxidation of *p*-xylene in its mixtures with the *o*-isomer on 1% Cu-ZSM-5 catalyst (390–450°). These reactions provide a good illustration of the molecular-sieve mechanism of the action of zeolites of the pentasil family, examined below.

5. Molecular-sieve Properties of Pentasils and the Selectivity of Reactions Taking Place on Them

Many examples of the molecular-sieve action of pentasils and the consequent high selectivity of the reactions are now known. These include the selective cracking of alkanes, the transformation of alcohols and lower alkenes to hydrocarbons containing not more than 10 carbon atoms in the chain, the absence in the products of these reactions of polyalkylbenzenes with branched side chains, condensed aromatic systems, etc. The most striking example is the selective formation of *p*-xylene in the isomerisation of xylenes, the disproportionation of toluene, and its alkylation by methanol.

It is possible to distinguish three types of molecular-sieve selectivity of zeolites[110,111], each of which is due to one of the following factors: 1) the size of the molecules of the original reagent, that is their ability to penetrate into the zeolite pores to the active centres localised in them; 2) the size of the molecules of the products, that is their ability to diffuse from the zeolite pores into the gas phase; and 3) the size of the intermediate complex, that is the possibility of the formation of this complex in the restricted space of the pores and cavities of the zeolite.

When the diameter of the zeolite channels is commensurate with the diameter of the molecules of the starting materials and the products, the reaction apparently takes place under internal-diffusion conditions, which may have a significant influence on the selectivity of the process[263]. The rate of diffusion of the molecules depends both on their size and on their shape or their ability to adopt a configuration which corresponds more closely to the size and shape of the zeolite channels. Under these conditions, which have been called "configurational diffusion" conditions[110], the selective formation of a definite reaction product may take place, that is there is "configurational selectivity".

The transformations of xylenes on pentasils take place under these conditions. Data on the composition and distribution of the reaction products, and also on the rate of the transformation of different xylene isomers[240,242,246] have shown that in this case all the above types of molecular-sieve selectivity are observed. Steric hindrance leads to a very marked decrease in the rate of the disproportionation of xylenes, but does not prevent their isomerisation, in which *p*-xylene is formed with a high selectivity. The molecules of this isomer, which has a smaller kinetic diameter (6.4–7.0 Å) than the molecules of *m*- and *o*-xylenes (6.9–7.6 Å), diffuse into the pentasil channels at the highest rate and readily migrate from the pores into the gas phase[70,84,87,110]. The molecules of *m*- and *o*-xylenes, which are present in the zeolite channels for a longer time, may undergo additional isomerisation into *p*-xylene, increasing the concentration of the latter in the reaction products. For zeolites with wider pores (for example mordenite[240]), the selective formation of *p*-xylene does not take place, since the molecules of all three isomers diffuse in the channels of this zeolite at approximately equal rates[240,242].

The influence of diffusion factors on the reaction rate is estimated using the dimensionless parameter $Q = [k(R^2/D)]^{1/2}$, where k is the reaction rate constant, R the radius of the zeolite crystallites, and D the effective diffusion coefficient of the molecules[110,263]. This parameter is related to the efficiency factor (η—the degree of utilisation of the internal surface of the catalyst) and to the configurational selectivity of the reaction ($S = D_p/D_a$, where D_p and D_a are the diffusion coefficients of the molecules p and a, which respectively diffuse easily and with difficulty into the zeolite pores).[111,263] A mathematical theory was recently developed for the selective formation of *p*-xylene in the isomerisation of xylenes, the disproportionation of toluene, and its alkylation by methanol under conditions of configurational diffusion on catalysts showing molecular-sieve properties[264].

The concept of the limiting role of the diffusion of the molecules in the pores of the zeolite makes it possible to explain the increase in the selectivity of *p*-xylene formation in various reactions on pentasils when partial coke formation takes place in the zeolite, when it is modified by various additives, or when the size of the crystallites increases. For example, the introduction of additives or partial coke formation in the zeolite during its operation leads to a decrease in the effective diameter of the channels and creates additional steric hindrance for the diffusion of molecules.

The modification of TsVK pentasil by vanadium decreases the sorptive capacity of the zeolite and the initial rate of adsorption for all three xylene isomers[211]. The sorption characteristics of the pentasil change to the smallest extent for *p*-xylene, however. In the alkylation of benzene by propylene on ultrasil pentasil[264], the change in the selectivity of the reaction with time is due to the accumulation in the zeolite channels of "condensation products" (that is coke or its precursors), which apparently restrict the access of the reacting molecules to the active centres.

It is also possible that when coke is formed in the pentasil or when various additives are introduced into it, the acidic properties of its surface may change, with a consequent change in the selectivity of the reactions. For example, when H-ZSM-5 zeolite is treated with phosphorus compounds, there is a marked increase in the number of surface acidic centres[158], and selective formation of *p*-xylene takes place on these zeolites[247,255]. According to data obtained by H–D exchange[208], however, modification of TsVK pentasil by vanadium does not lead to a change in the concentration of the surface OH groups, that is it has no influence on the acidic properties of the pentasil surface.

These data indicate the existence of a definite relationship between the selectivity of the reactions on pentasils, the nature of their porous structure, and the rate of diffusion of the molecules of the reagents and products in the zeolite pores. The question of the relationship between the acidity of zeolites and the selectivity of the reactions which they catalyse, and the influence of modifying additives on the acidic properties of the pentasils, is still not clear. A significant part in this relationship may be played by the nature of the additive, its localisation in the system of zeolite pores, and the state in which this additive may exist under the reaction conditions. Further studies are required in order to solve these problems, which are important for the directed control of the catalytic properties of zeolite catalysts.

V. THE USE OF PENTASILS IN OTHER CATALYTIC REACTIONS

A number of studies have shown that pentasils can be used as catalysts not only in the above transformations of oxygen-containing compounds and hydrocarbons, but also in various other reactions. Among these, an important place is occupied by processes directed towards the production of motor fuels from non-traditional raw materials, capable of replacing the petroleum products used for these purposes. A promising raw material in this respect is biomass (the waste products from the processing of agricultural products, the timber and timber-processing industries, etc.), on the basis of which a technological process has now been developed for the production of various synthetic fuels by thermochemical and fermentation processes[265–267]. The possibility in principle of using pentasils for the catalytic transformation of various components of plant raw materials into high-quality motor fuel was demonstrated[268] in a study of the transformations of polyisoprene latex, corn oil, castor oil, and other plant oils on ZSM-5 zeolite. At 450–500°, a high conversion of the starting materials was achieved, and the composition of the products was close to that of the hydrocarbon mixtures obtained from methanol, although they usually contained more benzene, toluene, and xylene.

The availability of zeolites of the pentasil family has provided a realistic solution to the problem of the production of motor oils from the products of the treatment of coal, including the conversion of synthesis gas[266,267,269–271]. Two versions of this process are usually considered:

$$\text{coal} \xrightarrow{+H_2O} CO + H_2 \begin{cases} \longrightarrow CH_3OH \rightarrow \text{petrol}; & (4) \\ \longrightarrow \text{petrol}. & (5) \end{cases}$$

Process (4) includes the intermediate formation of methanol, which can then be converted on a ZSM-5 zeolite into petrol, by the process developed by Mobil Oil (see section III). Method (5) is more attractive, since it makes it possible in principle to obtain petrol or individual hydrocarbons directly from synthesis gas without the intermediate stage. This process is complicated by the absence of catalysts giving a higher selectivity of the conversion of synthesis gas into hydrocarbons than the familiar catalysts of the Fischer–Tropsch process. Considerable progress has already been made in this direction, by using catalysts based on first-generation zeolites[272,273] and zeolites of the pentasil family[22,41,45,266,267].

The study of the conversion of synthesis gas on Fe-, Zn-Cr-, Zr-, or Co-zeolite catalysts of the ZSM-5 or ultrasil type, prepared by mixing or impregnation, showed that in the presence of a zeolite of the pentasil family there is a significant increase in the conversion of the original mixture and an increase in the yield of hydrocarbons, and aromatic hydrocarbons are formed[274–277]. In contrast to the usual versions of the Fischer–Tropsch process, the reaction products contained much smaller quantities of alkenes; the normal chains of the aliphatic hydrocarbons formed contained not more than 11 or 12 carbon atoms, and the aromatisation products consisted chiefly of benzene, toluene, and xylenes[274–277].

On a catalyst based on H-mordenite, but not pentasil, a decrease in the concentration of alkenes in the reaction products and the formation of aromatic hydrocarbons was also observed[276]. The conversion of synthesis gas, which was partly converted into CH_3OH and $(CH_3)_2O$, was ~4 times lower, however, than in the presence of pentasil. The nature of the metallic component has a significant influence on the catalyst properties. For example, the Zr- and Zn-Cr-ZSM-5 catalysts showed a much lower ability to give methane and a much higher aromatising power than the Fe-ZSM-5 catalyst[275].

The activity at 240° of the Co-ultrasil catalyst obtained by mixing depends on the SiO_2/Al_2O_3 ratio in the pentasil[276]. Increase in this ratio from 42 to 190 led to a decrease in the conversion of the synthesis gas, the total yield of hydrocarbons, and their concentration in the reaction products. At 190°, only a decrease in the proportion of hydrocarbons in the liquid catalysates was observed. The activity of the Co-ultrasil catalysts increased sharply when 3% MgO was added, but this led to a significant change in the composition of the reaction products, which contained C_1–C_{22} hydrocarbons. Increase in the concentration of the additive to 12% lowered the yield of the light C_5 and C_6 hydrocarbon fractions, increased the yield of C_7 and higher hydrocarbons, and suppressed the aromatisation. These additives had approximately the same effect on less active catalysts with the same composition (Co-ultrasil), prepared by impregnating the zeolite with cobalt carbonyl[276].

It is suggested[275] that on catalysts containing a zeolite of the pentasil family, the conversion of synthesis gas takes place according to the following scheme:

$$2H_2 + CO \xrightarrow{\text{metal}} [CH_3OH \rightleftarrows {}^1/_2 (CH_3)_2O + {}^1/_2 H_2O] \xrightarrow{\text{pentasil}} (CH_2) + H_2O .$$

The composition of the reaction products is determined both by the ability of the pentasil to transform the intermediate compounds (alcohol and ether) into hydrocarbons and also by its molecular-sieve properties, which prevent the formation

of long or bulky molecules. The influence of diffusion factors on the selectivity of the conversion of synthesis gas was studied with decrease in the size of the particles of the components of the Zn-Cr-ZSM-5 catalyst, that is with decrease in the path length of the molecules diffusing in the pentasil pores[275]. It is considered[274] that the active centres of the pentasil in the catalyst can interrupt the growth of the hydrocarbon chains by converting the α-alkene molecules into molecules which are inert with respect to the active centres of the metallic component (for example into aromatic hydrocarbons, branched and internal alkenes, etc.).

CO can be adsorbed on ultrasil-containing Co-catalysts of the Fischer–Tropsch synthesis in several forms, characterised by different temperatures of desorption (T_{des}).[276] With decrease in the Al concentration in the ultrasil there is a decrease in the total sorption of CO and an increase in the concentration of carbon monoxide adsorbed in a form with $T_{des} = 400°$, which apparently has the lowest activity in the synthesis of hydrocarbons. The lowest concentration of this form of adsorbed CO was detected for the most active catalyst containing Co-ultrasil + 6% MgO.

A catalyst based on ZSM-5 zeolite has been developed for transforming liquid oxidation products and various side products of the Fischer–Tropsch synthesis into more valuable aliphatic and aromatic hydrocarbons[278]. It has been shown possible to increase considerably the profitability of the Fischer–Tropsch process.

Mixed Co-ultrasil catalysts show a high activity in the carbon monoxide-initiated hydropolymerisation of ethylene, which gives mixtures of C_3–C_{22} hydrocarbons and ethane[279]. The activity of these catalysts decreased with decrease in the Al concentration in the zeolite. Unlike catalysts based on mordenite and zeolites of type Y, they retained their activity over a wide temperature range (190–310°) and gave products with a large proportion of C_5 and higher fractions. The products also contained aromatic hydrocarbons, and this was attributed to the influence of the pentasil. It was suggested[279] that the hydropolymerisation of ethylene is activated by carbon monoxide adsorbed on the zeolite surface.

One of the ways of using the products of the gasification of coal involves the use of carbon monoxide for the carbonylation of hydrocarbons to obtain carboxylic acids and their esters. It was previously shown that it is possible to carry out this reaction on heterogeneous non-zeolite catalysts containing Pd.[280–282] This reaction has also been studied on mordenite and TsVK pentasil containing group VIII metals[283,284]. The Pd-containing pentasils can be used as active catalysts for the production of propionic and butyric acids by the carbonylation of ethylene and propylene respectively.

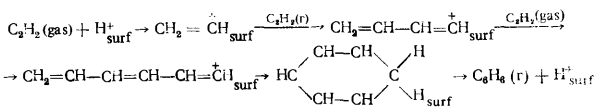
In the carbonylation of ethylene and propylene on catalysts based on pentasils, the formation of considerable quantities of esters such as ethyl propionate, isopropyl isobutyrate, and isopropyl n-butyrate has been observed[283, 284]. An interesting feature is that the H-form of a ZSM-5 pentasil showed no activity in the liquid-phase esterification of acetic acid by ethanol and isopropy alcohol[285].

The gas-phase chlorination of benzene (175°) on pentasils (NaH-ZSM-5, H-ZSM-5, Ce-ZSM-5, NaH-ZSM-11, and silicalite), and also on mordenite and amorphous SiO_2, gives chiefly chlorine addition products—a mixture of stereoisomers of hexachlorocyclohexane[286]. In contrast to this, the reactions on L and Ln-Y zeolites, and also on Al_2O_3, involved chiefly substitution to give chlorobenzenes containing up to 5 or 6 Cl atoms. It was suggested[286] that catalysts with a low Al concentration initiate the homolytic dissociation of chlorine, which is followed by its radical addition. Because of the large diameter of the molecules formed (~8 Å), this reaction apparently takes place only on the outer surface of the zeolite particles or in the openings into its pores.

In the hydrolysis of ethyl acetate (60°), it was shown possible to use pentasils, which have a hydrophobic surface, as catalysts for reactions in an aqueous medium[287]. In this reaction, H-ZSM-5 zeolite showed an activity equal to ~40% of the activity of a cation-exchange resin. Dealuminated mordenites were less active, and the original mordenite, zeolite Y, and amorphous aluminosilicates had a very low activity in this reaction. With increase in the atomic ratio Si/Al, the activity of all the zeolites studied increased, reached a maximum, and then decreased. Decrease in the quantity of Al in the zeolite is evidently accompanied by an increase in the hydrophobic character of its surface and an increase in its affinity for organic compounds. At a very low Al concentration, the zeolite loses its activity as a result of a decrease in the quantity of surface active centres on which the reaction takes place.

A zeolite of the pentasil family ($SiO_2/Al_2O_3 \cong 29$; 0.2 mass % Na_2O), not containing transition metals, can decompose ammonia at 550°.[288] Before the reaction, the zeolite was heated at a high temperature. The degree of dissociation of ammonia was ~42 mass %.

Data on the transformations of alkynes on pentasils are of interest[133,221,289]. For example, on Na- and H-ZSM-5 zeolites at temperatures above 300°, acetylene is very readily transformed (to the extent of more than 99%) into a mixture of C_6–C_{13} aromatic hydrocarbons[221]. Pure acetylene rapidly deactivates the catalyst, so that the reaction is carried out with dilution by an inert gas (He). The composition of the products depends on the volume rate of supply of acetylene. It is suggested[221] that the reaction involves the Brönsted acidic centres, with the intermediate formation of the vinyl cation and its homologues:



1,2-Dimethylacetylene readily undergoes cyclotrimerisation to hexamethylbenzene on ZSM-5 zeolite[133].

Examination of the above material shows that high-silica zeolites of the pentasil family in many respects are similar to the zeolites of the first generation. Because of their characteristic composition and structure, however, they are more stable to high temperatures, water vapour, and mineral acids, have a lower tendency to undergo cation exchange, and exhibit specific adsorption and catalytic properties.

Pentasils as catalysts are distinguished from zeolites of other types by their high stability, which is due to their low tendency to form coke, and their clearly defined molecular-sieve properties, which are responsible for the high selectivity of various reactions taking place on these zeolites. A characteristic feature of pentasils is their ability to transform methanol (and other oxygen-containing compounds) into hydrocarbon mixtures forming a high-octane petrol, to aromatise lower alkenes, and to catalyse various other reactions of practical interest. It may be expected that in the near future, zeolites of the pentasil family will provide a basis for the production of effective catalysts which will make it possible to solve the problem of producing motor fuels without using petroleum raw material, and also to obtain valuable chemical products from accessible and inexpensive starting materials.

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The Equilibrium NH Acidity of Organic Compounds

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The literature data of the last decade on the acidity of the N-H bond in organic compounds in aprotic solvents and in the gas phase are examined. The influence of structural factors on the equilibrium NH acidities of arylamines, carboxamides, sulphonamides, polyfluoroaryl compounds, and heterocycles, as well as the acidifying effects of the electron-accepting substituents at the NH acid centre are discussed on the basis of the results of studies of protolytic equilibria in dimethyl sulphoxide. The question of the influence of the *N*-anion stabilisation factors in solution (specific solvation and ion association) on the relative strengths of NH acids is also considered. Data obtained in studies of the NH acidity in the gas phase are presented.
The bibliography includes 103 references.

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I. INTRODUCTION

Organic compounds whose N–H bonds are involved in a protolytic equilibrium can be regarded as NH acids. They belong to the most common types of Brønsted acids in organic chemistry, like the CH and OH acids. However, in contrast to the latter, which have become the objects of numerous quantitative investigations[1–5], until recently few studies were made on NH acids[6]. Measurements of NH acidity have been used mainly to investigate the cationic forms, i.e. to estimate the basicity of nitrogen-containing compounds. The expansion of the sphere of preparative applications of NH acid anions (*N*-anions)[6] stimulated interest in the structural characteristics which determine the acidity of amino- or imino-group in organic compounds. In many respects they have been discovered in the course of systematic researches carried out during the last decade and to which this review is devoted.

The measure of the acidity of compounds in solution is the p*K*.[1,3] The acidity data are usually referred to the aqueous p*K* scale (pK_a), but, as a consequence of the hydrolysis of the *N*-anions, it is impossible to measure the p*K* of the majority of NH acids in aqueous solution and for this reason studies of the equilibrium NH acidity in non-aqueous media have acquired primary importance.

Considerable advances in the study of NH acids are associated with the application of the method based on the H_- function for media such as mixtures of water with hydrazine[7,8], sulpholan[9], and dimethyl sulphoxide[8–11] and also for alcohols[12,13]. The equilibrium NH acidities of many compounds have been investigated by the indicator method in liquid ammonia[14,15]. The results of these and other studies published up to 1972 have been included in a review[6] and will therefore not be considered here. We shall only mention that the differences between the properties of the solvents employed, their differentiating influence on the relative strengths of the NH acids, have been a serious obstacle to the establishment of a unique NH acidity scale. It was established in the course of studies of NH acids in aprotic polar solvents, in particular, in dimethyl sulphoxide.

II. THE EQUILIBRIUM NH ACIDITY OF ORGANIC COMPOUNDS IN DIMETHYL SULPHOXIDE

The first data on the equilibrium NH acidity of organic compounds in dimethyl sulphoxide (DMSO) were obtained as early as the second half of the 1960's,[10,16,17] while systematic studies of NH acids in DMSO have been carried out, starting from the middle 1970's, by Shatenshtein and co-workers[18–30] and Bordwell and co-workers[31–37]. Both groups of investigators have used the indicator method, based on the spectrophotometric determination of the equilibrium constant K_p of the proton transfer reaction from the NH acid (NH) to the indicator acid AH anion:

$$\rangle NH + A^- \rightleftharpoons \rangle N^- + AH \quad . \qquad (1)$$

The values of K_p, the p*K* of the indicator (pK_{AH}), and the p*K* of the test acid (pK_{NH}) are related:

$$\lg K_p = pK_{AH} - pK_{NH} \quad . \qquad (2)$$

The relation is used to calculate the pK_{NH} from the known values of pK_{AH}.

In the studies of Shatenshtein and co-workers the strengths of NH acids were estimated in terms of the relative acidity scale[38], on which the p*K* for 9-phenylfluorene, established[9] in aqueous sulpholan (18.5), served as a reference, while Bordwell and co-workers used in their studies an absolute scale[39] based on potentiometric data[40,41], on which p*K* = 17.9 corresponds to 9-phenylfluorene. Comparison of the two p*K* scales in dimethyl sulphoxide (DMSO) revealed the following discrepancies between them[42]: on average 0.3 of a logarithmic unit in the range p*K* > 20, 0.6 in the range 14 < p*K* < 20, and ~1.1 in the range p*K* < 14. We took into account these differences in comparing the data of the two groups of investigators. In the Tables below the p*K* are listed in terms of a scale on the basis of which the acidities of the majority of compounds of the given series have been established; together with the recalculated p*K*, the initial values are indicated in brackets.

The reaction centre in all NH acids (we have in mind neutral or anionic forms) is known to contain an unshared electron pair capable of conjugation with the π-electron system of the molecule. Evidently the greater the degree of conjugation and of the delocalisation of the electrons of the unshared pair, the stronger the resonance effects of the substituents at the nitrogen atom on the energy state of the second unshared pair liberated in the heterolytic dissociation of the N–H bond. At the same time, their role in the stabilisation of *N*-anions, one of the unshared pairs in which occupies the σ orbital, is apparently less pronounced than the role of the inductive effects and is not as great as in the stabilisation of carbanions having an analogous structure. Bearing in mind this preliminary remark, we shall consider the influence of structural factors on the equilibrium NH acidity of organic compounds. In the case of acyclic NH acids of the type ArNHR, we shall discuss mainly the effect of substituents in the aryl group Ar and of the groups R directly linked to the acid centre. In the case of heterocyclic NH acids attention will be concentrated on the influence of the structure of the heterocycle and of the substituents in the latter or in the annelated benzene ring.

1. Aniline, Diphenylamine, and Their Substituted Derivatives

Substituted anilines and diphenylamines, particularly the nitro-derivatives, are widely used as indicators in the study of acid–base equilibria and it is therefore useful to quote the full compilation of their p*K* determined in DMSO. The majority of data (Table 1) have been obtained by Bordwell and co-workers, who were the first to measure directly the p*K* of aniline [compound (II)] in DMSO. The acidities of certain other compounds, namely (VIII), (XVIII), (XXII), and (XXIII), were measured in other investigations[43,44] in a buffered system containing phenylacetylene as the proton-donating additive in DMSO. The p*K* found for the NH acids (IV), (IX), (XIII), (XVI), and (XX) are smaller by 1–3 logarithmic units than the values established by Bordwell (see Bordwell et al.[35] concerning the discrepancy) and there is a satisfactory linear relation between the two sets of data ($r = 0.999$), which we used to recalculate in terms of the absolute scale the p*K* determined in a buffer solution. p*K* values similar to those quoted in Table 1 have been obtained for diphenylamine (XXI) (24.8 on the absolute scale[19]) and compounds (XVI), (XVII), (XX), and (XXIV) (potentiometric titration with tetrabutylammonium hydroxide[45]). At the same time, for certain substituted anilines [compounds (XVI), (XVII), and (XX)], Bordwell and co-workers found higher p*K* values than in previous studies[10,16,17,40], in which unduly high estimates were apparently obtained for these and a number of other NH acids in DMSO.

An excellent correlation of the p*K* of aniline and its *meta*-substituted derivatives [compounds (I)–(VII)] and the Hammett σ constants has been obtained ($\rho = 5.67$; $r = 0.9996$),[33] and it is satisfied also by the p*K* of compounds (VIII), (X), (XI), and (XV) (for the last three compounds, values of $\sigma^- = 1.05$, 1.00, and 1.65 respectively must be used[46]). However, the p*K* of 4-benzoyl- and 4-nitro-anilines deviate significantly from the linear relation towards higher acidities even when nucleophilic constants are used.

The available information about the acidities of substituted diphenylamines in DMSO is so far extremely scanty. An approximate estimate of the sensitivity of the NH group of diphenylamine to the electronic influence of the substituents in one benzene ring, based on the three compounds (XXI) to (XXIII), yields $\rho = 4.60$ for the Hammett relation when a nucleophilic constant is used for the nitro-group.

The relative acidities of a large series of polynitrodiphenylamines (17 compounds) have been measured in dimethylformamide (DMF) by potentiometric titration (using tetrabutylammonium hydroxide in methanol as the titrant)[47]. The p*K* found vary in the range from 11.3 for 4′-methoxy-2,4,2′-trinitrodiphenylamine to 1.28 for 2,4,6,2′,4′,6′-hexanitrodiphenylamine. The acidity of 2,4-dinitrodiphenylamine was estimated by extrapolating the relation between the p*K* and Σσ for certain polynitrodiphenylamines and p*K* = 12.65 was obtained. It differs little from the p*K* measured in DMSO [cf. compound (XXIV) in Table 1], which justifies the assumption that the data of Sharnin et al.[47] are a good approximation to the absolute p*K* scale for NH acids in DMSO. For a series of 4′-substituted 2,4,2′-trinitrodiphenylamines, there is a satisfactory correlation between the p*K* and the Hammett σ constants ($r = 0.999$; $n = 5$). The specificity of the effect of the *ortho*-nitro-groups has also been noted; whereas the first is somewhat inferior in its acidifying influence to the *para*-nitro-group, the second appreciably surpasses the analogous *para*-substituent in this respect.

Table 1. The equilibrium NH acidities of aniline, diphenylamine, and their substituted derivatives in DMSO (absolute p*K* scale[39]).

Compound	Substituent	p*K*	Refs.	Compound	Substituent	p*K*	Refs.
Substituted anilines							
(I)	3-CH_3	31.0	[33]	(XI)	4-CN	25.3	[33]
(II)	H	30.7	[31]	(XII)	4-$C_6H_5SO_2$	24.9	[33]
(III)	3-CH_3O	30.5	[33]	(XIII)	2,6-Cl_2	24.8	[35]
(IV)	3-C	28.5	[33]	(XIV)	4-C_6H_5CO	24.4	[33]
((V)	3-B	28.4	[33]	(XV)	4-CF_3SO_2	21.8	[33]
(VI)	3-CF_3	28.2	[33]	(XVI)	4-NO_2	20.9	[33]
(VII)	3-CN	27.5	[33]	(XVII)	4-Cl, 2-NO_2	18.9	[36]
(VIII)	3,4-Cl_2	27.1 (24.5)	[44]	(XVIII)	2,5-Cl_2, 4-NO_2	17.5 (16.2)	[43]
(IX)	2,4-Cl_2	26.2	[35]	(XIX)	2,6-Cl_2, 4-NO_2	17.4	[35]
(X)	4-CH_3SO_2	25.6	[33]	(XX)	2,4-$(NO_2)_2$	15.9	[35]
Substituted diphenylamines							
(XXI)	H	24.95	[36]	(XXIII)	4-NO_2	19.2 (17.7)	[43]
XXII)	3-Cl	23.5	[43]	(XXIV)	2,4-$(NO_2)_2$	12.4 (13.5)	[24]

2. Aminoazines

The data on the acidities of aminoazines in DMSO (Table 2) and aniline made it possible to estimate reliably the acidifying effects of the aza-groups in various positions in the heterocycle (these positions are designated by a numeral in brackets): 3.1 (2), 2.4 (3), and 4.5 (4) logarithmic units (within the limits of ±0.2 of a logarithmic unit)[28]. As a rule, in the presence of several groups, their effects are additive except for two aza-groups in the *ortho*-positions relative to an amino-group in a side chain [compounds (XXIX) and (XXXIV)]; their combined effect is smaller by 0.8–1.0 of a logarithmic unit than the value calculated assuming additivity[28]. It has been suggested that the deviation from additivity is due to the destabilising influence of the free electron pairs of the *ortho*-nitrogen atoms, which cannot be located simultaneously in the *trans*-positions relative to the electron pair of the imino-nitrogen atom, liberated when the proton of the N–H bond is abstracted.

For a series of NH acids, including the aminoazines (XXV) to (XXVIII) and (XXX)–(XXXIII) and aniline, a correlation equation ($r = 0.998$), linking the p*K* to the relative values of

the σ constants of the aza-groups (σ_N), found from the acidifying effects, has been found[28]. Using the ratio of ρ for the given correlation (4.16) to that for substituted anilines (see above), the relative constants σ_N were adjusted to the scale of the Hammett constants: 0.55 (σ_{2N}), 0.44 (σ_{3N}), and 0.78 (σ_{4N}).[48] They are smaller than the corresponding values of σ_N established in water[49,50], because in DMSO there is no possibility for the specific solvation of aminoazines and their *N*-anions (for the formation of a hydrogen bond with the endocyclic nitrogen atoms), which could enhance the electron-accepting properties of the azine ring in a proton-donating medium.

Table 2. The equilibrium NH acidities of aminoazines in DMSO [28] (relative scale[38]).

Compound	Name	p*K*
(XXV)	3-Aminopyridine	28.9
(XXVI)	2-Aminopyridine	28.0
(XXVII)	4-Aminopyridine	26.7
(XXVIII)	5-Aminopyrimidine	26.4
(XXIX)	2-Aminopyrimidine	25.9
(XXX)	2-Aminopyrazine	25.8
(XXXI)	3-Aminopyridazine	25.7
(XXXII)	4-Aminopyridazine	24.1
(XXXIII)	4-Aminopyrimidine	23.9
(XXXIV)	2-Amino-*sym*-triazine	21.5

The influence of substituents in the heterocycle on the NH acidity of aminopyrimidines has been studied in fair detail[23]. It has been established that π-donor groups as a rule deviate from the linear relation between the p*K* and the Hammett constants. The results of a two-parameter correlation analysis (with subdivision of the σ into σ_I and σ_R) have shown that, when the endocyclic nitrogen atom is located between the substituent and the amino-group [the 4-substituted derivatives of compound (XXIX) or the 2-substituted derivatives of compounds (XXXIII)], the electronic effects are transmitted via the pyrimidine ring to a greater extent than via the benzene ring. For the *para*-positions of the substituent and the amino-group, there are conditions for direct polar conjugation (σ_R^- is used in the correlation instead of σ_R), but, if the substituent is then in the *ortho*-position relative to both aza-groups [2-substituted derivatives of compound (XXVIII)], then the best correlation between the p*K* and the Hammett constants is achieved for resonance components represented by the sum $0.6\sigma_R + 0.4\,\sigma_R^-$.

In conclusion, we may note that it is possible to obtain a unique correlation equation describing the dependence of the p*K* on the sum of the Hammett constants (including the values of σ_N presented above) and embracing the 3- and 4-substituted anilines (I)–(VIII), (X), (XI), and (XV), the aminoazines (XXV)–(XXVIII) and (XXX)–(XXXIV), and the majority of the substituted derivatives of compounds (XXVIII) and (XXXIII):[48]

$$pK = 31.0 - 5.38\Sigma\sigma \quad (S = 0.36;\ r = 0.993;\ n = 44)\ .$$

3. Carbonyl Compounds

Data for the equilibrium NH acidities of carbonyl compounds of the type RCONHR′ in DMSO are listed in Table 3. Comparison of the p*K* for carboxamides and arylamines with a similar structure shows that the CO group has a considerable acidifying effect [cf., for example, the p*K* of aniline (II) and compounds (XL)–(XLV)] and appreciably reduces the sensitivity of the acid centre to the electronic effect of the second α-substituent (R′). Thus, whereas the acidities of aniline and 4-aminopyridine exceed the acidity of ammonia (p*K* = 41 in DMSO [34]) by 10 and 14 logarithmic units respectively, the acidities of acetamide (XXXVII) and its phenyl- and 4-pyridyl-substituted derivatives (XL) and (XLVIII) differ by only 4 and 6.5 logarithmic units respectively. The influence of the CO group is manifested also by a weakening of the transmission of the effects of substituents via the benzene ring to the N–H bond. Thus the following values of ρ have been obtained for the three series of NH acids of the type $RCONHC_6H_4X$ in DMSO for the relations between the p*K* and the Hammett constants of the substituents X (the number of the compound corresponding to X = H is indicated in brackets; in all the series $r = 0.995$): −3.22 (XLIV);[26] −3.16 (XLIII);[19] −2.96 (XLVII);[18] in absolute magnitude, they are all smaller than ρ for substituted anilines (see above).

Table 3. The equilibrium NH acidities of the carbonyl compounds RCONHR′ in DMSO (relative scale).

Compound	R	R′	p*K*	Refs.
(XXXV)	NH_2	H	26.6 (25.1) *	[17]
(XXXVI)	$(CH_3)_3C$	H	26.0 (25.7)	[32]
(XXXVII)	CH_3	H	25.8 (25.5)	[32]
(XXXVIII)	H	H	23.8 (23.5)	[32]
(XXXIX)	C_6H_5	H	23.7 (23.4)	[31]
(XL)	CH_3	C_6H_5	21.8 (21.5)	[31]
(XLI)	C_6H_5NH	C_6H_5	20.9	[26]
(XLII)	$(CH_3)_2CHCH_2O$	C_6H_5	20.7	[19]
(XLIII)	CH_3O	C_6H_5	20.3	[19]
(XLIV)	$C_6H_5NCH_3$	C_6H_5	19.9	[26]
(XLV)	H	C_6H_5	19.7	[27]
(XLVI)	C_6H_5	NH_2	19.5 (18.9)	[36]
(XLVII)	C_6H_5	C_6H_5	19.3 **	[18]
(XLVIII)	CH_3	C_5H_4N ***	19.2	[27]
(XLIX)	$(CH_3)_2CHCH_2S$	C_6H_5	17.4	[19]
(L)	C_6H_5	C_5H_4N ***	17.1	[27]
(LI)	CCl_3	C_6H_5	13.4	[27]
(LII)	CN	C_6H_5	12.5	[26]

*Recalculated[17] taking into account the difference between the p*K* of urea (XXXV) and diphenylamine.
**19.4 (18.8).[31]
***4-Pyridyl.

In connection with the study of the effects of substituents in the benzene ring, we may point out that the p*K* of 4-fluoro-derivatives of acetanilide and formanilide (21.3 and 19.4)[27] and of a series of 2′-substituted benzanilides[18] have also been determined in DMSO. In particular, it has been shown that the influence of the 2′- and 4′-nitro groups on the NH acidity of benzanilide (XLVII) is virtually the same (the p*K* of the substituted derivatives are 15.5 and 15.4 respectively[18]); this has also been observed for *N*-phenylcarbamate (XLIII).

The nature of the substituent R at the carbon atom of the CO group also has appreciable influence on the strength of the carbonyl NH acids [cf., for example, the p*K* of compounds (XL), (XLV), (XLVII), (XLIX), (LI), and (LII)]. The correlation between the p*K* and the Taft σ* constants (ρ* = 4.69; $r = 0.997$) for substituents R, which are mainly alkyl and chloroalkyl groups, has been obtained for the chloralamides $CCl_3CH(OH)NHCOR$ whose acidity has been measured

potentiometrically in a mixture of benzene and methanol[51]. The inductive influence of R is a decisive factor also in the NH acidity of dichlorovinylamides $CCl_2 = CHNHCOR$ (R = alkyl, chloroalkyl, phenyl, or substituted phenyl; potentiometric measurements in DMF; $\rho^* = 2.36$; $r = 0.996$).[52] A linear relation of a similar kind has also been established for the carboxamides $R''CH_2CONH_2$ (R'' = H, F, C_6H_5O, CH_3O, C_6H_5, C_6H_5S, etc.; $\rho^* = 2.8$; $r = 0.908$),[32] but, for R'' = alkyl, no correlation is observed between the pK and σ^*.[32]

On the other hand, certain data in Table 3 also cannot be interpreted from the standpoint of the predominant inductive influence of the substituent R on the acidity. If that were so, urea (XXXV) should be a more acid compound than acetamide (XXXVII) and *N*-phenylcarbamate (XLVII) should be more acid than formanilide (XLV). Since the actual relative strengths of the above NH acids are the reverse of expectation, the hypothesis that the π-donor capacity of the substituents R (for example, NH_2 and CH_3O) also plays an appreciable role suggests itself. A confirmation of this may be seen in the two-parameter correlations

$$pK = 24.3 - 9.1\sigma_I - 4.7\sigma_R^- \quad (S = 0.4;\ r = 0.971),$$
$$pK = 20.1 - 9.7\sigma_I - 4.9\sigma_R^- \quad (S = 0.12;\ r = 0.999),$$

deduced for the $RCONH_2$ [compounds (XXXV)–(XXXIX)] and $RCONHC_6H_5$ [compounds (XL), (XLIII), (XLV), (XLVII), and (LII)] series respectively, from which it follows that, apart from the inductive contribution to R to the stabilisation of *N*-anions, account must be taken also of its resonance effect.

The influence of substituents in the benzene ring attached to the CO group on the NH acidity has been investigated in relation to benzanilides. The relative pK of compounds having the general formula $4\text{-}XC_6H_4CONHC_6H_4OCH{=}CH_2$ were determined potentiometrically in DMF, pyridine, and other solvents and linear relations between the pK and the Hammett constants of the substituents X were established (the values of ρ vary from −6.18 to −7.85 depending on the medium)[53].

The replacement of the oxygen atom in the CO group by sulphur entails an increase of the NH acidity by 4–6 logarithmic units, which follows from a comparison of the pK of urea[15,17] or *N*-phenylcarbamate[19] and their thio-analogues. The acidities of certain thiocarbonyl compounds have been investigated potentiometrically in DMF, in which the pK of the thioamides $4\text{-}XC_6H_4NHCSR$ (R contains a CH group linked to powerful electron acceptors—the CN, $C_6H_5SO_2$, etc. groups)[54] and the acylthioureas RCONHCSNHR′ (R = 2-furyl substituted in the 5-position or 4-substituted phenyl; R′ = phenyl or 4-substituted phenyl) were determined[55,56]. In the case of thioamides the second dissociation constant corresponds to the ionisation of the N–H bond (the first refers to the C–H bond); the range of variation is small: from 0.8 to 1.6 logarithmic units on passing from X = H to $X = NO_2$ for different R.

In the series where $R = CH(SO_2C_6H_4Cl\text{-}4)CONH_2$ the pK are correlated with the σ^0 constants of the substituents X ($\rho = -1.95$). Only one dissociation step, attributed to the N–H bond between the CO and CS groups, has been noted for acylthioureas (the terminal NH group forms a hydrogen bond with the oxygen atom of the CO group[55]). The influence of the nature of the substituents in the furan or benzene ring (for $R' = C_6H_5$) on the NH acidity of acylthioureas is more appreciable than in the thioamides indicated above: the values of ρ in the Hammett relations are respectively −6.8 and −5.3. In the series where R = 2-furyl and $R' = C_6H_4X$ the sensitivity of the acid centre to the effects of the substituents X is fairly low: the pK vary in the range 8.9–11.3 [$X = 2\text{-}NO_2$ and $4\text{-}(C_2H_5)_2N$ respectively] and for the 3- and 4-substituted derivatives it was not possible to discover a dependence of pK on the Hammett constants.

4. Sulphonamides

The equilibrium NH acidity of sulphonamides (Table 4) is lower by 6–7 logarithmic units than that of their carbonyl analogues (cf. Table 3). This large difference is due to the fact that, in terms of the negative inductive effect $-I$, which plays the most important role in the stabilisation of *N*-anions, the SO_2 group is significantly superior to the CO group. Accordingly, the acidifying influence of the substituents R at the sulphur atom in the RSO_2 group on the N–H bond is apparently also even more inductive in its character than the influence of the analogous substituents on the N–H bond in carboxamides. In particular, we may note that the pK of sulphonamides of the type RSO_2NH_2 [compounds (LIV), (LVII), and (LXI)] vary linearly with the Taft constants of the substituents R, including the phenyl group:

$$pK = 18.3 - 2.86\sigma^* \quad (r = 0.998).$$

Alkyl substituents at the nitrogen atom of benzenesulphonamide reduce the NH acidity in conformity with their inductive effects[27] [see compounds (LIII) and (LV)–(LVIII)].

Table 4. The equilibrium NH acidities of the sulphonamides RSO_2NHR' in DMSO (relative scale.

Compound	R	R′	pK	Refs.
(LIII)	C_6H_5	$(CH_3)_3C$	18.2	[27]
(LIV)	CH_3	H	18.1 (17.5)	[31]
(LV)	C_6H_5	$(CH_3)_2CH$	17.9	[27]
(LVI)	C_6H_5	C_2H_5	17.7	[27]
(LVII)	C_6H_5	CH_3	17.5	[27]
(LVIII) *	C_6H_5	H	16.8	[27]
(LIX)	C_6H_5	C_6H_5	12.6	[27]
(LX)	C_6H_5	C_5H_4N **	11.3	[27]
(LXI)	CF_3	H	10.8 (9.7)	[31]
(LXII)	CF_3	C_6H_5	6.8 (5.7)	[36]

*pK = 16.7 (16.1) has been quoted[37] for compound (LVIII).
**4-Pyridyl.

The acidities of benzenesulphonanilides substituted in the benzene ring attached to the nitrogen atom are described by a linear correlation between the pK and the Hammett constants ($\rho = -2.7$ and $r = 0.990$ for the *meta*- and *para*-substituents and $\rho = -2.53$ and $r = 0.998$ for the *ortho*-substituents[27]).

5. Polyfluoroaryl-substituted Compounds

The complete substitution of hydrogen atoms by fluorine in the aryl groups of arylamines or carboxamides is accompanied by an increase of the equilibrium NH acidity by 6–8 logarithmic units [cf. the pK of compounds [LXIII)–(LXVII) in Table 5, compounds (II), (XXVII), (XXI), (XL), and (XLVII) in Tables 1–3, and compounds (LXV) and (LXVIII) in Table 5]. The high electron-accepting capacity of the polyfluoroaryl groups is due to the negative inductive effect of fluorine atoms[57]. Like the sulphonyl group, they therefore activate the N–H bond to a greater extent than the carbonyl group and are superior in this respect also to the *p*-nitrophenyl group[24].

The equilibrium NH acidity of compounds C_6F_5NHAr is described satisfactorily by a two-parameter correlation equation, where the chemical shift δ_F of the signal of the *para*-fluorine atom of the C_6F_5 group in the ^{19}F NMR spectra has

been suggested as a measure of the resonance influence of the aryl group Ar: [24]

$$pK = 20.0 - 3.88\sigma^* + 0.36\delta_F \quad (r = 0.988) .$$

Table 5. The equilibrium NH acidities of polyfluoroaryl-substituted compounds C_6F_5NHR in DMSO [24] (relative scale).

Compound	R	pK
(LXIII)	H	23.1
(LXIV)*	H	19.2
(LXV)	C_6H_5	19.2
(LXVI)	CH_3CO	15.5
(LXVII)	C_6H_5CO	13.0
(LXVIII)	C_6F_5	12.6
(LXIX)	$C_{10}F_7$**	11.8
(LXX)	C_6F_5CO	10.8
(LXXI)	$2,4\text{-}(NO_2)_2C_6H_3$	10.2***
(LXXII)	C_5F_4N	9.4

*Instead of the C_6F_5 group, compound (LXIV) contains the 2,3,5,6-tetrafluoropyridyl group C_5F_4N.
**2-Heptafluoronaphthyl.
***Taken from Vlasov et al.[29]

Table 6. The acidifying effects (ΔpK) of the substituents R in NH acids.

R	I	II	III
C_6H_5	10.3	5.8	3,9
CH_3CO	15.5	9.2	7,6
HCO	17.5	11.6	—
C_6H_5CO	17.6	11.9	10.1
C_6F_5	18.2	11.8	10.5
CN	24.0	—	—
$C_6H_5SO_2$	24.9	19.2	—
$2,4\text{-}(NO_2)_2C_6H_3$	25.1	18.3	12.9
CF_3SO_2	31.3	25.0	—

Note. The ΔpK were found as the differences between the pK of ammonia [~41 (Algrim et al.[34]), series I], aniline [30.7 (Bordwell and Algrim[31]), series II], and pentafluoraniline [22.8 (Vlasov et al.[24]), series III], on the one hand, and the pK of the corresponding *N*-substituted derivatives on the absolute scale; apart from the data in Tables 1–5, $pK = 17.0$ for cyanamide[37] has been used.

Satisfactory linear relations ($r = 0.988–0.998$) between the pK and the Hammett constants for the substituents X have been obtained for four series of NH acids of the type $4\text{-}XC_6F_4NHR$ (dialkylamino-groups, which exhibit an extremely weak electron-donating effect in the above series, were not included in the correlation). The constants ρ vary as follows (the substituents R are indicated in brackets)[29]: -6.43(H); -3.93(C_6F_5); -3.23(C_6H_5CO); -3.01[$2,4\text{-}(NO_2)_2C_6H_3$]. The differences between them and the ρ in the correlations for the analogous series of non-fluorinated compounds (see above) are insignificant, i.e. the degree of transmission of the electronic effects of the *para*-substituents via the benzene ring to the NH acid centre changes little when the *ortho*- and *meta*-hydrogen atoms are replaced by fluorine[29]. This is also supported by the results of a quantum-chemical calculation (by the CNDO/2 method) of the parameters of the highest occupied molecular orbital in the *N*-anions containing the phenyl or pentafluorophenyl group at the nitrogen atom[29].

6. The Acidifying Effects of the Substituents in Acyclic NH Acids

In conclusion of the discussion of data for the equilibrium NH acidity of acyclic compounds in DMSO, it is useful to compare the acidifying effects of α-substituents, which provide a clear idea about the relative strengths of NH acids of different types. Table 6 presents the values of ΔpK characterising the acidifying influence of a series of groups on the N–H bonds of ammonia, aniline, and pentafluoroaniline.

The sequence in which the ΔpK vary is virtually the same in all three series and there is a linear relation between the ΔpK for series I and II:

$$\Delta pK_I = 1.06\Delta pK_{II} + 5.1 \quad (S = 0.6;\ r = 0.996) .$$

On the other hand, the absolute magnitude of the acidifying effect of a given substituent decreases from series I to series II and further to series III. This can be partly due to the increased steric hindrance to the conjugation of the substituent R with the nitrogen atom on replacement of a single hydrogen atom in ammonia by the phenyl (series II) and pentafluorophenyl (series III) groups. However, this is not the only cause and apparently not the main cause of the inconstancy of the ΔpK noted above. For example, the steric environments of the acid centres in aniline and 4-aminopyridine are identical and yet the acidifying effects of the CH_3CO, C_6H_5CO, and $C_6H_5SO_2$ groups in aniline are greater by 1–3 orders of magnitude than in aminopyridine [cf. the differences between the pK of compound (XXVII) and compounds (XLVIII), (L), and (LX) with the corresponding ΔpK in series II]. Furthermore, the steric hindrance should not be reflected in the stabilisation of the *N*-anions via the inductive mechanism and yet the tendency towards a decrease of the ΔpK can be distinctly traced also for substituents which exert a predominantly inductive influence on the N–H Bond (C_6F_5, $C_6H_5SO_2$, and CF_3SO_2).

An analogous situation has been observed for the CH acidity[58,59] and has been interpreted as a consequence of the mutual weakening of the electronic effects of the substituents at the acid centre[34,42]. Evidently this phenomenon is of a general character and must be taken into account also in the consideration of the NH acidity†.

7. Nitrogen-containing Heterocycles

The principal data on the acidity in DMSO of heterocycles containing the imino-group in the ring are presented in Table 7. The majority of the NH acids of this type are azoles and their derivatives. The equilibrium NH acidity of azoles increases with increase in the number of aza-groups in the ring and the influence of such groups in the β-positions on the N–H bond is greater than that of those in the α-positions [cf. the pK of compound (LXXIX) and those of (LXXXII) and (LXXXIV) or the pK of the last two compounds and (LXXXIX), Table 7].

† New values of the constants σ^-, whereby one can take into account the influence of the substituents in CH acids, have been proposed recently[60], but it is not possible to obtain even a satisfactory linear relation between these constants and the pK of NH acids measured in DMSO.

The influence of the ring substituents on the acidity of azoles is predominantly inductive. Thus a linear relation has been obtained between the pK of 2-substituted and 2,3-disubstituted pyrroles and the sum of the inductive constants σ_I of the substituents ($\rho = -17.4$; $r = 0.994$) and the transmission of the effect of the substituent from the 3-position is twice as weak as the transmission of the effect from the 2-position[22]. The acidity of substituted pyrazoles and imidazoles can be described by correlations between the pK and the sum of the constants σ_m regardless of the number of substituents and their positions in the ring ($\rho = -8.8$ and -9.5 and $r = 0.987$ and 0.999 respectively)[21].

Table 7. The equilibrium NH acidities of nitrogen-containing heterocycles in DMSO (relative scale).

Compound	Name	pK	Refs.
(LXXIII)	1,2,3,4-Tetrahydroquinoline	32.1	[20]
(LXXIV)	1,2,3,4-Tetrahydroquinoxaline	32.1	[20]
(LXXV)	Indoline	30.5	[20]
(LXXVI)	2,2-Pentamethylenebenzimidazoline	29.3	[20]
(LXXVII)	3,4-Dihydro-2*H*-benzo-1,4-thiazine	28.8	[20]
(LXXVIII)	Acridan	25.2	[30]
(LXXIX)	Pyrrole	23.3	[21]
(LXXX)	Phenothiazine	22.8	[21]
(LXXXI)	Indole	21.3	[21]
(LXXXII)	Pyrazole	20.4	[21]
(LXXXIII)	Carbazole	19.6	[21]
(LXXXIV)	Imidazole	18.9	[21]
(LXXXV)	Indazole	18.8	[21]
(LXXXVI)	Phenanthridinone	18.3	[30]
(LXXXVII)	Benzimidazole	18.1	[21]
(LXXXVIII)	9-Acridone	16.4	[30]
(LXXXIX)	1,2,4-Triazole	15.4	[21]
(XC)	Benzotriazole	12.6	[21]
(XCI)	Tetrazole	9.3 (8.2)	[36]

Note. The statistical correction for two NH groups has been introduced for compounds (LXXIV) and (LXXVI). For compounds (LXXIX) and (LXXXI), Bordwell et al.[37] obtained similar pK values, equal to 23.35 (23.05) and 21.25 (20.95) respectively, while for compound (LXXXIII) a higher pK, amounting to 20.5 (19.9), was obtained.

When the azole ring is annelated to the benzene ring, the NH acidity increases on average by two logarithmic units. A satisfactory linear relation ($r = 0.995$) has been established between the pK of compounds (LXXIX), (LXXXI), (LXXXII), (LXXXIV), 2-phenylimidazole, and their benzo-derivatives; with its aid, the acidity of 1,2,3-triazole (pK = 14.7) has been estimated from the pK of benzotriazole[21]. The influence of the benzo-group should apparently be attributed to the strengthening of the delocalisation of the unshared pair of the electrons of the "pyrrole" nitrogen atom over the π-electron system of the molecule, although one cannot rule out the possibility that the inductive effect of the sp^2-hybridised carbon atoms of the benzo-group also plays an appreciable role. In this connection one may note that the inductive effect of the phenyl group in the 2-position of pyrrole increases the NH acidity by 1.7 logarithmic units[22].

However, the role of conjugation in the stabilisation of the N-anions of certain heterocycles is apparently nevertheless greater than in the case of acyclic NH acids. Structural changes which affect the p,π-conjugation system in the molecules of azoles can lead to an appreciable weakening of the NH acidity. Thus the rupture of the o,o'-C–C bond between the benzene rings of carbazole (LXXXIII) or its replacement by a methylene bridge, is accompanied by a decrease of acidity by more than 5 logarithmic units [cf. with diphenylamine (XXI) in Table 1 or with acridan (LXXVIII)]. The consequences of a decrease in the size of the π-electron system of benzoheterocycles and of the "dearomatisation" of the heterocyclic ring following its partial hydrogenation at the C=C or C=N bond are even more appreciable (10–12 logarithmic units) [cf. the pK of compounds (LXXV) and (LXXXI) and of (LXXVI) and (LXXXVII)]. On the other hand, the annelation of the benzoheterocycles (LXXIII) and (LXXVII) to a second benzene ring with simultaneous replacement of the aliphatic C–C bond by an aromatic bond leads virtually to a doubling of the size of the π-electron system and the consequent increase in the NH acidity by 6–7 logarithmic units [cf. with compounds (LXXVIII) and (LXXX)]. The analogous structural change in the case of a five-membered heterocycle is accompanied by an increase of the NH acidity by 11 logarithmic units [cf. compounds (LXXV) and (LXXXIII)].

When the methylene group of acridan is replaced by the carbonyl group, the NH acidity increases by ~9 logarithmic units [cf. with 9-acridone (LXXXVIII)], which is close to the acidifying effect of the acyl groups in aniline (9–12 logarithmic units—see Table 6, series II). In view of the considerable remoteness of the acid centre of 9-acridone from the CO group, presumably the contribution of its inductive effect to the stabilisation of the given N-anion is smaller than in acyclic carbonyl-containing N-anions. The planar conformation of the 9-acridone molecule apparently favours the manifestation of the resonance effect of the CO group, which is the maximum possible for NH acids. It has been suggested that this is the reason why the sensitivity of the acid centre of 9-acridone to the resonance influence of substituents in the 2-position (the *para*-position relative to the nitrogen atom) is weakened[30].

The benzoheterocyclic compounds (LXXIII)–(LXXVII) with a partially reduced heterocyclic ring can be regarded by convention as the corresponding *ortho*-substituted N-alkylanilines. It is not therefore surprising that their acidities are similar to that of aniline. It is remarkable that the acidity of compounds with a five-membered heterocycle is appreciably higher than that of their six-membered analogues [cf. compounds (LXXIII) and (LXXV), (LXXIV), and (LXXVI)]. This difference persists also for their p-nitro-substituted derivatives (when the nitro-group is introduced, the acidity increases by 10–12 units)[20]. This behaviour was first observed in a potentiometric determination of the NH acidities of anthraquinones containing the imino-group in the annelated five- or six-membered heterocycle (the range of the pK for the compounds investigated is from 11.4 to 20.7).[61] The increase of acidity following a decrease in the size of the heterocycle has been explained by the increase of the s character of the orbital of the N–H bond as a consequence of the endeavour of the nitrogen atom to rehybridise due to the tendency of the five-membered ring annelated to the benzene ring to weaken the strain.

The above data exhaust the information currently available about the influence of the structure of organic compounds on the acidity of the N–H bond in DMSO. Measurements of the pK of NH acids in other aprotic solvents (mainly in dimethylformamide[47,52–54], nitromethane[62,63], and a number of others) covered a much smaller number of compounds and did not yield fundamentally new information about the influence of the structure of the compounds on their equilibrium NH acidity compared with data for solutions in DMSO.[64] On the other hand, the relative strengths of the NH acids frequently change significantly on passing from proton-donating to relatively non-polar solvents, which is due primarily to

factors stabilising *N*-anions such as specific solvation or association with the counterion[42,65].

Studies of NH acids using proton-donating media (water, alcohols, mixtures of DMSO with hydroxylated components, etc.) are being prosecuted at the present time. Thus a number of investigations of the NH acidities of arylamines[50,66,67], derivatives of guanine[68] and barbituric acid[69], and certain azoles[70,71] in the above solvents have been published during the last 5–7 years. The equilibrium NH acidities of certain heterocycles and carbonyl compounds have been measured also in a weakly polar aprotic solvent—1,2-dimethoxyethane[18,19,21,72]. It is therefore of interest to consider to what extent the differences between the proton-donating capacities or polarities of the solvents are reflected in the strength of the NH acids.

III. THE INFLUENCE OF THE MEDIUM ON THE STRENGTH OF NH ACIDS

The overall pattern in the change of the equilibrium NH acidity of organic compounds when DMSO is replaced by water is illustrated in Fig.1, where the p*K* for NH acids of different structural types, determined relative to the corresponding standard states in both solvents, are compared. The pK_a employed (the subscript *a* indicates the assignment of the p*K* to the acidity scale in aqueous solutions[3]) were either measured directly in water or were obtained by the authors[50,73] by recalculating the values for mixed solvents using methods taking into account the activities of the species involved in the protolytic equilibrium. It has been shown for a large number of CH and NH acids that the results of the recalculation by two such methods[78,79] are in good agreement[80].

Analysis of the relation between the p*K* of NH acids in both solvents shows easily that the equilibrium NH acidities of the majority of compounds in DMSO are lower than in water—the circles in Fig.1 are distributed mainly above the dashed straight line passing through the origin of coordinates at an angle of 45°. This difference has come to be explained by the fact that, by virtue of the specific character of the solvation in water (the formation of hydrogen bonds), the *N*-anions are stabilised in this solvent to a greater extent than in DMSO. The reduced NH acidity in DMSO is partly, but apparently to a lesser extent, caused by the formation of stronger hydrogen bonds between the molecules of the NH acids and the solvent (see Trofimov et al.[22] and Karjalainen and Ruostesno[81] concerning this topic) whose basicity is higher than that of water[39]. For *N*-anions with a highly delocalised charge, the degree of specific solvation in water is diminished, while the solvation of the anion in DMSO via the dispersion interaction mechanism is actually enhanced[40,41]. This is probably why the NH acidities of the corresponding compounds, for example, of 2,4-dinitrodiphenylamine (see point 14 in Fig.1), are higher in DMSO than in water.

The data presented in Fig.1 also show that, when the solvent is changed, the strengths of the NH acids change unequally: the differences between the pK_{DMSO} and pK_a vary from 2.5 to 6 logarithmic units, i.e. a differentiating effect of the medium on the equilibrium NH acidity is observed. At the same time, linear relations between both parameters can be found for structurally similar NH acids (see the straight line in Fig.1 and the data in Table 8).

The pK_{DMSO} and the pK_a of anilines and unsubstituted aminoazines (Table 8, series I and II) are correlated most effectively and the form of the linear relation I hardly changes when aniline and diphenylamines are combined into a single series (cf. series I and II). The considerable scatter of the points in the case of azoles (see points 21–28 in Fig.1) precludes a conclusion concerning a distinct linear relation between pK_{DMSO} and pK_a. One can only speak of a parallel variation of these quantities. Relations with a satisfactory correlation coefficient and standard deviations greatly superior to the accuracy of the determination of the p*K*, which is to within 0.1, can be obtained for monocyclic azoles (series IV) and benzazoles (series V). The excellent linear correlation obtained for benzenesulphonanilides (series VI) is appreciably impaired when benzenesulphonamide (series VII) is included in the above series. On the basis of the foregoing, one can conclude that the solvation effects responsible for the shift of the protolytic equilibrium on replacement of an aprotic solvent by a proton-donating solvent depend specifically on the structure of the NH acid. At the same time their contributions to the energetics of the acid dissociation process vary in proportion in a series of NH acids of a given structural type.

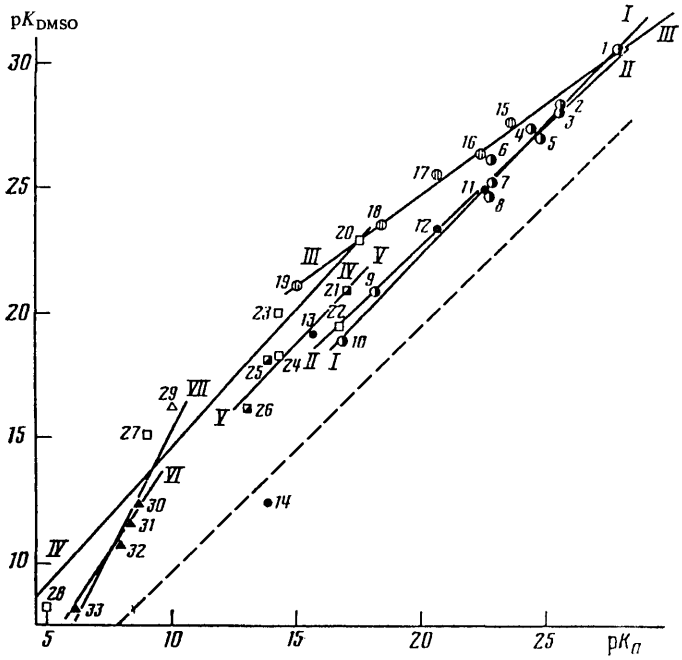


Figure 1. The equilibrium NH acidities of organic compounds in dimethyl sulphoxide (pK_{DMSO}) and in water (pK_a) (the pK_a are indicated in brackets); aniline and its substituted derivatives[73] (the substituents are indicated): 1) H (27.8); 2) 3-Cl (25.5); 3) 3-CF_3 (25.4); 4) 3-CN (24.3); 5) 3,4-Cl_2 (24.6)l 6) 2,4-Cl_2 (22.6); 7) 4-CN (22.7); 8) 2,6-Cl_2 (22.6); 9) 4-NO_2 (18.1); 10) 4-Cl, 2-NO_2 (16.8); diphenylamine and its substituted derivatives[73]: 11) H (22.4); 12) 3-Cl (20.6); 13) 4-NO_2 (15.5); 14) 2,4-$(NO_2)_2$ (13.8); aminoazines[50]: 15) 2-aminopyridine (23.5); 16) 4-aminopyridine (22.3); 17) 2-aminopyrimidine (20.5); 18) 4-aminopyrimidine (18.4); 19) 2-amino-*sym*-triazine (14.9); azoles: 20) pyrrole (17.5);[74] 21) indole (17.0);[75] 22) carbazole (16.7);[76] 23) pyrazole (14.2);[74] 24) imidazole (14.2);[74] 25) indazole (13.8);[75] 26) benzimidazole (12.9);[75] 27) 1,2,4-triazole (8.9);[70] 28) tetrazole (5.0);[70,71] 29) benzenesulphonamide (10.0) [77] and benzenesulphonanilides[77] (the substituent in the 4'-position is indicated); 30) CH_3 (8.7); 31) H (8.3); 32) Cl (7.9); 33) NO_2 (6.2).

It is also of interest to note the following factors. The regression coefficient *b* in the correlation equation (Table 8) shows that, when the solvent is replaced, the sensitivity of the acid centre in compounds of the given structural type to the electronic effects of the substituents is altered. In particular, for phenyl-substituted NH acid (series I, II, and VI), the coefficient *b* is determined by the ratio of the constants ρ of the Hammett relations between the p*K* and σ in DMSO and in water (it has been assumed that the Hammett σ constants are identical for the two solvents). In the majority of the series of NH acids considered the coefficient *b* exceeds unity, which indicates a smaller sensitivity of the NH acidity to structural factors in the aqueous solution (cf., for example, the values of ρ for substituted anilines—$\rho = 5.20$ in water[50] and $\rho = 5.67$ in DMSO [34]). As a result of this, the replacement of DMSO by water entails a smoothing out of the differences between the NH acid strengths within a given series.

Table 8. Correlations of the type $pK_{DMSO} = a + bpK_a$ for NH acids in different structural series.

Series	Compound	*a*	*b*	*S*	*r*	*n*
I	Anilines (Nos. 1-10)	1.5±1.3	1.05±0.06	0.4	0.994	10
II	Anilines and diphenylamines (Nos. 1-13)	3.0±0.9	0.99±0.04	0.5	0.991	13
III	Aminoazines (Nos. 1 and 15-19)	10.1±0.4	0.74±0.02	0.2	0.998	6
IV	Azoles (Nos. 20, 23, 24, 27, and 28)	3.6±1.7	1.12±0.13	1.3	0.979	5
V	Benzazoles (Nos. 21, 25, and 26)	2.6±3.5	1.09±0.24	0.7	0.976	3
VI	Benzenesulphonanilides (Nos. 30-33)	−2.2±0.8	1.65±0.1	0.2	0.996	4
VII	Benzenesulphonamides (Nos. 29-33)	−5.3±0.7	2.07±0.08	0.7	0.979	5

Note. The numbers of the series correspond to the numbers of the straight lines in Fig.1, while the numbers of the compounds correspond to the numbers of the points in the same Figure.

Such levelling of the acidity in a hydroxylated solvent can be explained by the specific solvation of *N*-anions. The higher the basicity of the *N*-anion (the greater the p*K* of its conjugate NH acid), the stronger the hydrogen bond between it and the solvating molecules of the hydroxylated solvent and the greater the decrease of the p*K* on passing from DMSO to a proton-donating medium. Thus the coefficient *b* can be regarded also as a measure of the sensitivity of *N*-anions to the stabilising effect of specific solvation. Judging from the data in Table 8, it is a maximum for sulphonamides (series VI and VII), which is probably due to the involvement of the oxygen atoms of the SO_2 group in the formation of hydrogen bonds.

Series III, in which the regression coefficient is significantly less than unity, attracts attention in this connection. This implies that an "anomalous" tendency is observed for unsubstituted aminoazines—the levelling of acidity on passing from water to an aprotic medium. The most probable cause of this anomaly is specific solvation of the aminoazine anions at the endocyclic nitrogen atoms, which enhances the electron-accepting influence of the latter on the acid centre (indeed, as mentioned earlier, the Hammett constants for the aza-groups in water are larger than for the same groups in DMSO [48]). This factor is apparently more important than the decrease of the sensitivity of the anionic centre to the effects of the aza-groups in water (decrease of ρ) and the difference between pK_{DMSO} and pK_a therefore increases with increasing sensitivity of the aminoazines, in contrast to what is observed for other NH acids.

An analogous phenomenon can probably occur also for azoles. For example, the difference between pK_{DMSO} and pK_a (i.e. ΔpK) increases with increase of acidity in the sequence pyrroles (5.5) < pyrazole (5.8) < triazole (6.2) (Fig.1). However, there is no doubt that the actual situation may be more than complex because the pyrazole and triazole anions each contain two equivalent nitrogen atoms, which function as both anionic centres and substituents simultaneously.

We shall now consider how the change from a polar to a weakly polar medium is reflected in the relative strengths of NH acids. In a weakly polar medium the protolytic equilibrium involves species resulting from the association of the free anions with the counterion (M^+), in particular ion pairs, and not the free ions themselves (Eqn.(1)):[42,82]

$$\rangle NH + A^-M^+ \rightleftharpoons \rangle N^-M^+ + AH\,. \qquad (3)$$

The pK_{NH} calculated by Eqn.(2) from the equilibrium constant of reaction (3) characterises the so-called "ion-pair" acidity (pK_p) and is related to the "free-ion" (pK_i) value of pK_{NH} determined for equilibrium (1):

$$pK_p = pK_i - \lg (K_{AM}/K_{NM}) \qquad (4)$$

where K_{AM} and K_{NM} are the dissociation constants of the ion pairs A^-M^+ and $\rangle N^-M^+$ into free ions. Evidently the stronger the association of the *N*-anion with the counterion (other conditions being equal) the greater the displacement of equilibrium (3), the greater the difference between pK_p and pK_i, and the greater the relative strength of the conjugate NH acid.

The effectis of ion association have been investigated in detail for CH acids[83-86], for which appreciable differences between the pK_i, measured in DMSO, and the pK_p, determined relative to the same standard in 1,2-dimethoxyethane (DME), have been established in many instances. The difference is particularly large (up to 8 logarithmic units) when the CH acid molecule contains a heteroatom (nitrogen or oxygen) to which there is a partial transfer of the anionic charge on ionisation of the C–H bond. The coordination of the counterions to such "hard" nucleophilic centres takes place with formation in DME of very stable contact ion pairs (for the varieties of the latter, see Szwarc[87]).

An analogous study has been carried out also for NH acids: the pK_p have been determined in DME for ~20 compounds, incorporating the Li^+ or Cs^+ counterions, relative to 9-phenylfluorene ($pK = 18.5$).[72] It has been shown that they are appreciably smaller than the corresponding pK_p, measured in DMSO and for Li^+ the difference between the pK values is greater than for Cs^+, since in the contact ion pair the anion is stabilised to a greater extent than the cation with a smaller radius. Since a "hard" nucleophilic centre (the nitrogen atom) is already present in *N*-anions, the introduction of other heteroatoms into such species is not accompanied by such an appreciable differentiation of the equilibrium "ion-pair" acidity as for the CH acids with analogous structures. Furthermore, satisfactory linear relations have been obtained for the entire set of NH acids investigated in DME:

$$pK_p(Li^+) = 0.89\,pK_i - 2.6 \quad (S = 1.0;\ r = 0.971)\,,$$
$$pK_p(Cs^+) = 1.01\,pK_i - 1.5 \quad (S = 0.6;\ r = 0.992)\,.$$

In the first equation the regreession coefficient is significantly less than unity, which indicates an enhancement of the stabilising effect of the lithium cation with increase of the intrinsic basicity of the *N*-anions. In the case of a

weaker interionic interaction (with the caesium cation), the stabilising effect of the counterion hardly changes in the acidity range investigated (18 logarithmic units).

The K_{NM} (M = Cs) in DME have been determined conductimetrically for a series of compounds (diphenylamine, carbazole, nitrophenyl-substituted NH acids, and certain others) and the pK_i in DME have been calculated by Eqn.(4).[72] The majority of the constants are slightly (by 0.3–0.5 of a logarithmic unit) smaller than the corresponding pK_i in DMSO, but the differences for the nitro-derivatives reach 1.4–1.9 logarithmic units. Such an appreciable difference can be a consequence both of the marked stabilisation of the nitrophenyl-substituted NH acids in the more basic DMSO and of the relatively less effective solvation of the corresponding *N*-anions in this solvent. At any rate, these results show that differentiation of the NH acid strengths is observed in protic solvents, but it does not occur for the analogous CH acids[42,82].

Thus our comparison of the quantitative data for the equilibrium NH acidities of organic compounds in media differing in their polar and proton-donating properties shows that specific solvation and ion association have a differentiating effect on the stability of their *N*-anions in solution. As a result of this, the available information about the NH acid strengths in a hydroxylated or weakly polar solvent can give rise to a distorted idea about the true structural rules governing the equilibrium NH acidity. In order to discover such rules, one can employ the NH acidity scale in DMSO or a similar p*K* scale established in a weakly polar solvent (for example in DME) with a counterion having a large radius (Cs^+). The most reliable information about the influence of the structure of compounds on their acidity is provided by the results of studies of protolytic equilibria in the gas phase.

IV. NH ACIDITY IN THE GAS PHASE

Studies of equilibria involving proton transfer in the gas phase have been prosecuted quite vigorously during the last decade. The usefulness of such research is undoubted because it gives rise to the possibility of separating the purely structural effects in acidity from the solvation effects[88]. However, as in the condensed phase, the main objects of investigations have been OH and CH acids. Data concerning the gas phase NH acidities of organic compounds are so far scanty and studies have been made mainly on the cationic forms of NH acids: alkylamines[89–92] and substituted pyridines[93] and anilines[94]. The results of such investigations have been analysed in fair detail in two reviews[88,95], which have been supplemented by an extensive communication by Taft and co-workers[96].

The relative strengths of the neutral forms of NH acids in the gas phase were first compared by Brauman and Blair[97], who established the following sequence in which acidity varies in the series of primary and secondary aliphatic amines: Et_2NH > t-$BuCH_2NH_2$ ≧ t-$BuNH_2$ ≧ Me_2NH ≧ iso-$PrNH_2$ > $PrNH_2$ > $EtNH_2$ > $MeNH_2$ > NH_3. Later Mackay et al.[98] determined the free energies ΔG of abstraction of a proton from the N–H bond in certain amines (Table 9) and showed that the acidity of amines is higher than that of ammonia. Thus it follows from the data presented that alkyl groups, which are usually regarded as electron donors, exhibit electron-accepting properties in the gas phase, stabilising amide anions. According to the above investigators[97,98], the stabilisation is due to the interaction between the negatively charged nitrogen atom and the polarisable alkyl group.

The ΔG for a series of other NH acids have been found by Kebarle and co-workers[100,101]. Having observed that the acidity of diacetamide is lower than that of its CH analogue, namely acetylacetone, the above investigators suggested that the ΔG found for barbituric acid (327.3 kcal mol^{-1})[100] characterises the acidity of the CH_2 group, while the energy of the deprotonation of the N–H bond should be somewhat higher (by ~2 kcal mol^{-1}). McIver and co-workers[99,102] determined the difference $\delta\Delta G$ in the gas phase between the ΔG for *p*-xylene (adopted as the standard acid), on the one hand, and pyrrole, aniline, and phenyl-substituted anilines, on the other. According to their estimate, $\delta\Delta G$ for the pair of NH acids methylamine and aniline is 35.9 kcal mol^{-1}, which makes it possible to calculate the ΔG indicated for aniline in Table 9 (we may note that ΔG = 353 kcal mol^{-1} has been obtained for pyrrole by an analogous procedure; cf. Table 9).

Table 9. The free energies of the deprotonation (ΔG) of certain NH acids in the gas phase.

Compound	ΔG, kcal mol^{-1}	*T*, K	Refs.
Ammonia	396.1	298	[98]
Methylamine	395.7	298	[98]
Ethylamine	391.7	298	[98]
Dimethylamine	389.2	298	[98]
Aniline	359.8	320	[99]
Pyrrole	351.8	300	[100]
Acetanilide	345.8	300	[100]
Acetylurea	341.1	300	[100]
Diacetamide	339.8	300	[100]
Succinimide	338.0	300	[100]

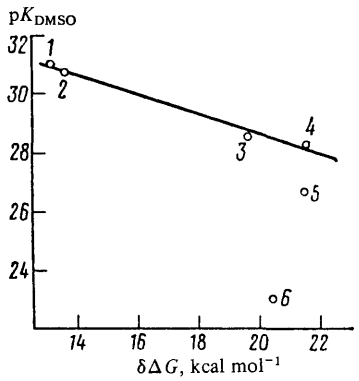


Figure 2. The equilibrium NH acidities of compounds in the gas phase (the relative deprotonation energies $\delta\Delta G$) and in DMSO (pK_{DMSO}): 1) 3-methylaniline; 2) aniline; 3) 3-chloroaniline; 4) 3-trifluoromethylaniline; 5) acetanilide; 6) pyrrole (according to the data in Tables 1, 3, 7, and 9).

It has been shown[99] that the $\delta\Delta G$ for *meta*- and *para*-substituted anilines are satisfactorily correlated with the Hammett σ constants (ρ = 10.4), but the points for the 3-F, 4-MeO, and 4-CF_3 substituents then deviate significantly from the straight line (r = 0.948). On the other hand, the two-parameter relations obtained for both series of substituted

anilines using the σ_I and σ_R^- constants are characterised by a high correlation coefficient (0.991). Bartmess et al.[99] note that the effects of the substituents are greater in the gas phase than in solutions. For example, in liquid ammonia and DMSO the parameters ρ of the Hammett relations (5.3 and 5.7 respectively) are smaller almost by a factor of two than in the gas phase (10.4). Furthermore, the ratio ρ_R^-/ρ_I for *meta*-substituted compounds decreases and that for *para*-substituted compounds increases on passing from the gas phase to the condensed phase.

For substituted anilines, a satisfactory agreement is observed between the acidities in the gas phase and in DMSO,[99] while in other cases there is an inversion of the acidity sequence (cf., for example, acetanilide and pyrrole in Fig. 2). Consequently an appreciable superposition of solvation effects on structural effects cannot be ruled out even in an aprotic solvent. The view according to which the rules governing the variation of the "intrinsic" acidity (i.e. the acidity determined only by the molecular structure) of compounds can be established only by methods for the investigation of gas-phase proton-transfer processes is therefore apparently quite valid[88].

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In conclusion we may note that the expansion of studies on protolytic equilibrium in the gas phase and in an aprotic medium is in our view quite promising. The result of such investigations not only make it possible to obtain the correct idea about the relation between NH acidity and the structure of a compound but also one can solve the practically important problem of the quantitative estimation of solvation effects, including the effect of specific solvation, in acid–base interactions. The study of processes involving the transfer of a proton in the N–H bond in the excited states of acid and conjugate base molecules is of both theoretical and practical interest[103].

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Conformational Analysis of Phosphoryl Compounds with Phosphorus-Carbon Bonds

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The literature data on the conformational analysis of phosphoryl compounds containing one or several phosphorus-carbon bonds are analysed. Attention is concentrated to the steric orientation of the phosphoryl group and the substituents at the α-carbon atom. Data concerning different phase states of the compounds are discussed. The necessity for a combined application of various physicochemical methods to the solution of conformational problems involving complex phosphoryl compounds in solution is emphasised.
The bibliography includes 121 references.

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I. INTRODUCTION

Organic compounds containing the phosphoryl group have found extensive applications as complex-forming agents. In particular, such derivatives are used to synthesise new medicinal drugs effective in the elimination of toxic metal ions from the organism and in technological processes for the separation and concentration of the most valuable metals[1]. Phosphates and their derivatives play a key role in biochemical processes as structural elements in many biological components and as energy transferring agents, which is associated with their ability to form complexes with the so-called "metals of life"[2,3].

The importance of the class of compounds under consideration can be explained in the first place by the significant electron-donating capacity of the oxygen atom in the phosphoryl group—an effective centre for the formation of complexes with various metal ions. Data on the steric structures of the ligands, characterised by the bond length and the valence and dihedral angles, as well as information concerning the changes in the potential energy of the system occurring as a result of internal rotations are very important for the elucidation of the complex formation reaction mechanisms. These factors are in fact responsible for the growing interest in the stereochemical properties of phosphoryl compounds. We may note that the approaches to the theoretical analysis of the steric effects in complex formation and the results of the study of the complex-forming properties of polydentate ligands containing phosphoryl groups have been discussed in a number of communications[4-6].

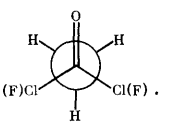
During the last decade vigorous studies have been made on the conformational analysis of phosphoryl compounds, but the complete analysis of the results obtained has not yet been carried out. The earlier reviews[7,8] include data obtained up to the end of the 1960s. In the monograph of Vilkov et al.,[9] the available data on the properties of phosphoryl compounds are described in an extremely concise form. The review of Bokii et al.[10] discusses only data obtained by X-ray diffraction while that of Arshinova[11] deals with data secured by the dipole moment and Kerr effect methods.

In the present review an attempt has been made to summarise the results of experimental and theoretical studies on the conformational properties of phosphoryl compounds with phosphorus–carbon bonds carried out in recent years. The review presents a logical analysis of the steric structures of compounds as a function of the character of the substituents at the phosphorus and carbon bonds.

II. HINDERED INTERNAL ROTATION ABOUT A SINGLE P–C_{sp^3} BOND

1. Alkylphosphonic Acid Dihalides

We shall discuss initially the conformational properties of compounds of the $\begin{matrix}R_1\\ \\ R_2\end{matrix}\!\!>\!P(O)Alk$ series using as examples the dichloride $Cl_2P(O)CH_3$ (I) and difluoride $F_2P(O)CH_3$ (II) of methylphosphonic acid. Reliable structural data, obtained by electron diffraction, are available for compound (I) in the gas phase[12]. According to these results[12], the angles at the phosphorus atom deviate significantly from tetrahedral values: $\angle O{=}P{-}C = 117.4° \pm 1.0°$, $\angle O{=}P{-}Cl = 114.5° \pm 0.5°$, $\angle CH_3{-}P{-}Cl = 103° \pm 0.5°$, and $\angle Cl{-}P{-}Cl = 101.8°$ (calculated). Because all three atoms attached to the carbon atom are identical, the hindered internal rotation involves the formation of only one triply degenerate staggered conformation:



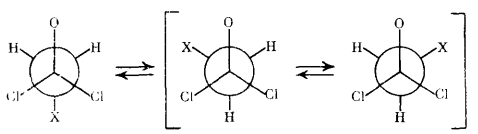
No information whatever has been published[12] concerning the character of the hindered internal rotation.

An effective method for conformational analysis is that of vibrational spectroscopy, which can yield information about the conformation mobility and the character of the changes in potential energy as a result of internal rotation. There have been a number of publications on the vibrational spectra of compounds (I) and (II) in different states of aggregation[13-22]. Thus, Durig and co-workers[18,19] analysed in detail the infrared and Raman spectra of compound (I) in gaseous, liquid, and solid states. The identification of the bands in the vibrational spectra was based on the available

literature assignments for related compounds. However, Durig et al.[18] were unable to isolate the torsional vibrations. Using improved infrared and Raman spectroscopic techniques, Durig and Casper[19] obtained clear-cut spectra of compounds (I) and (II) in the range 33–300 cm^{-1}. Having assigned specific lines and bands in this part of the spectra to torsional frequencies, the authors calculated the potential barriers to the rotation of the methyl groups in both compounds. Since this information is very important for the characterisation of intramolecular interactions, we shall consider in greater detail the interpretation of the experimental data obtained in the above study.

Eight bands were observed in the far infrared spectrum of a crystalline specimen of compound (I)[19]. Since five of these bands did not undergo any changes in frequency on raising the temperature from −190° to −80°C, the authors assigned them to intramolecular vibrations. Four of them, split into doublets (for specimens in the crystalline state), were assigned, by analogy with earlier studies[18,20], to different deformation vibrations. The "superfluous" fifth band at 264 cm^{-1} was assigned to a torsional vibration and the potential barrier was estimated from its frequency. Evidently, this approach is not rigorous without calculations for the vibrations. Furthermore, when torsional frequencies are employed, the correspondence between the mode of the observed vibration and that of the purely torsional vibration[21] and an exact estimate of the inertial parameters of the torsional vibration[22] are important. Finally, even for a correct estimate of the barrier, it is not clear to what type of interactions the characteristic obtained should be assigned. The neglect of the intermolecular interactions and of the crystal field effects can lead to a significant distortion of the true intramolecular component.

The replacement of even one hydrogen atom in the CH_3 group by some other substituent can lead to the appearance of different conformers and to equilibrium between them. Assuming that the presence of the barrier corresponds to conformations with eclipsed bonds, three stable staggered conformations can be put forward for compounds having the formula $Hal_2P(O)CH_2X$ (where X = alkyl):



The vibrational spectra of the compound $CH_3CH_2P(O)Cl_2$ (III, X = CH_3) have been discussed in a whole series of publications. Infrared absorption bands and Raman lines in the spectra of a liquid specimen of compound (III) were first interpreted by Gerding and Maarsen[13]. Analysis of the causes of the appearance of the $\nu_s(PCl_2)$ doublet led to the conclusion that a mixture of isomers is produced. The doublet in the range 1250–1300 cm^{-1} was assigned to the resonance of the Fermi stretching vibration of the phosphoryl linkage and the deformation vibration of the C–H bond. Although the above study[13] was in fact quoted in subsequent reports[23–25], the cause of the appearance of a doublet in the range 1250–1300 cm^{-1} was not discussed; the question of equilibrium between the conformers is interpreted in the same way as in the earlier investigation[13]. Steger and Kuntze[24] indicated a specific structure of the conformers (*gauche*- and *trans*-orientations of the P=O and C–C bonds). The available data concerning the assignment of the bands and lines to specific type of vibrations are extremely contradictory.

In later communications[26–28] there are no references to the earlier data[13,25]. It has been stated[26] that the study of the infrared spectra of compound (III) confirmed the conclusions reached by Steger and Kuntze[24]. Shagidullin et al.[27] estimated the thermodynamic parameters of the equilibrium involving the conformers of compound (III) in a non-polar medium (solvent—carbon tetrachloride, temperature 298 K). An estimate of ΔH for compound (III) has also been published by Fishman and Remizov[28], but it refers to a liquid specimen and the energy of the conformers includes in this instance intermolecular interactions. The above workers[28] estimated the height of the barrier to the internal rotation of compound (III) from the torsional frequency quoted by Steger and Kuntze[24]. $\Delta H_{trans\text{-}gauche}$ = 0.1 kcal mol^{-1} has been obtained for compound (III).[27]

The initial data concerning the structure of the compound $Cl_2P(O)CH(CH_3)_2$ (IV) were contradictory. Thus, in their study of the vibrational spectra of compound (IV), Gerding and Maarsen[13] did not observe signs of a conformational equilibrium. Christol and Christol[23] postulated equilibrium between two conformers on the basis of the doublet band assigned to the antisymmetric vibrations of the PCl_2 group.

Comparison of the infrared and Raman spectra of compound (IV) in various media and at different temperatures[29,30] permitted a more specific conclusion concerning its structure. It was found that equilibrium between two conformers is characteristic of this compound, as for the ethyl derivative. The thermodynamic parameters of the equilibrium were calculated from the temperature variation of the spectra of compound (IV) in solution (solvent—n-hexane, temperature 182–298 K): $\Delta H_{gauche,gauche/trans,trans} = -0.5$ kcal mol^{-1}, $\Delta F = -0.2$ kcal mol^{-1}, and $\Delta S = -1.0$ kcal mol^{-1} K^{-1}.[30]

The substitution of all three hydrogen atoms at the α-carbon atom by CH_3 groups to give the compound $Cl_2P(O)C(CH_3)_3$ (V) also results in the stabilisation of the triply degenerate conformation by the hindered internal rotation. The barrier to the hindered internal rotation about the P–C bond in compound (V) is then greater than in compound (I) owing to the increased repulsion between the non-bonded atoms. The ^1H NMR spectra of compound (V) have been analysed[31,32]. Nixon and Schmutzler[32] did not observe any signs of hindered internal rotation about the P–C bond, but, on the basis of the broadening of the signals of the methyl protons on cooling the specimen, Bushweller and Brunelle[33] postulated the possibility of a barrier having a height of 7 ± 1 kcal mol^{-1}.

The dipole moment (DM) and Kerr effect methods and vibrational and ^1H NMR spectroscopic data were used in the identification of the steric structures of the conformers of compounds (III)–(V) formed[30] [the ^1H NMR spectra of the liquid compound (III), (IV), and (V) have also been published by Siddall and Prohaska[34]]. It was established on the basis of the Kerr constants that equilibrium between conformers with the *trans*- and *gauche*-dispositions of the P=O and C–CH_3 groups in proportions of 0.35:0.65 is characteristic of compound (III) in solution in CCl_4 at 298 K, while equilibrium with the *trans,gauche*- and *gauche,gauche* dispositions in proportions of 0.4:0.6 is characteristic of compound (IV). ^1H NMR spectroscopic data obtained under the same experimental conditions have led to the conclusion that there is equilibrium between the above conformers in proportions of 0.25:0.75 and 0.45:0.55. Thus the conclusions concerning the structure of the conformers and the quantitative estimates of the equilibrium positions for compounds (III) and (IV) obtained on the basis of infrared and ^1H NMR spectroscopic measurements agree, the latter to within 5%.

The NQR spectroscopic method has been resorted to in order to reach a conclusion about the conformations of compound (I), (II), and (IV) in the crystalline phase. It was established that symmetrical and asymmetric conformations are stabilised in the crystal cells of compounds (III) and (IV) respectively[35,36], which agrees with vibrational spectroscopic data for compound (III)[27] but conflicts with other results[30]. The NQR frequencies quoted[35,36] apparently do not allow in the given instance a reliable identification of the structure of the compound. In particular, a splitting of the signal by approximately 0.3 Hz has been observed for compound (I), which has a symmetrical structure, i.e. the splitting is of the same order of magnitude as that which has been attributed to the non-equivalent states of the two chlorine atoms owing to their different environments in other derivatives.

Spectroscopic data indicating a considerable structural similarity of phosphoryl, thiophosphoryl, and selenophosphoryl derivatives are also available for the analogous compounds with P=S and P=Se bonds. In particular, detailed studies have been made of the compounds $Cl_2P(S)C_2H_5$ (VI)[30,37,38] and $Cl_2P(S)C_3H_7$ (VII)[37], which led to the detection of conformational equilibria for these compounds in the liquid state.

The spectra of compound (I), (III)–(V), and $Cl_2P(O)Bu^i$so (VIII) in the range 400–700 cm^{-1}, in which infrared absorption bands and Raman lines assigned to the stretching vibrations of the P–Cl bond are observed, have been compared[29,30]. Only two bands or lines (symmetrical and antisymmetric vibrations of the PCl_2 group) are observed for compounds (I), (V), and (VIII) in the above range under the experimental conditions (solutions of different polarity, temperature 180–300 K), which indicates the absence of a dynamic equilibrium between two conformers of compound (VIII) and the existence of a conformer with the *gauche*-disposition of the bulky substituent at the α-carbon atom relative to the P=O bond. The authors[29,30] explained this by the increase of the energy of the *trans*-orientation of the P=O and isobutyl groups owing to steric interactions. The conclusion reached has also been confirmed by the agreement between the frequencies ν_s and ν_{as} of the vibrations of the PCl_2 group in the spectrum of compound (VIII), on the one hand, and the components of the ν_s and ν_{as} doublets of the PCl_2 group in the thoroughly investigated compound (III), on the other. The character of the infrared and Raman spectra of compounds (I) and (V) is consistent with the existing view concerning their structure; the infrared spectra of compound (V) have also been published by Holmes and Fild[39].

In order to elucidate the character of the intramolecular effects, Raevskii et al.[30] carried out calculations for non-valence interactions within the framework of the atom–atom approximation. The calculations yielded somewhat high interaction energies. Thus the height of the barrier to internal rotation in compound (V) proved to be twice as high as in the study of Bushweller and Brunelle[33]. However, the character of the change in energy in the course of internal rotation was determined correctly[30]: the potential energy minima correspond to the *gauche*- and *trans*-dispositions of the $C-CH_3$ and P=O groups; a deeper minimum corresponds to the *gauche*-conformer of compound (III) and the *gauche*, *gauche*-conformer of compound (IV). It is noteworthy that, from the standpoint of steric non-valence interaction, the preference for the *gauche*-position compared with the *trans*-position in the case of the hindered internal rotation about the P–C bond is partly due to the deviations of the valence angles involving the phosphorus atom from the tetrahedral value[7]. On passing from compound (III) to compound (IV), there is an increase in the energy difference between the conformers, which has also been observed experimentally. A slight increase of energy compared with the skewed structure results from the CH_3 group being eclipsed by the oxygen atom of the phosphoryl group. The barrier corresponding to the conformation with eclipsed P–Cl and $C-CH_3$ bonds is found to be fairly high.

Thus the steric interactions of the non-bonded atoms determine the character of the changes in the potential energy curves in the course of internal rotation about the $P-C_{sp^3}$ bond in compounds (I)–(VI).

2. Phosphoryl and Thiophosphoryl Compounds with a Single Halogen or Cyanoalkyl Group

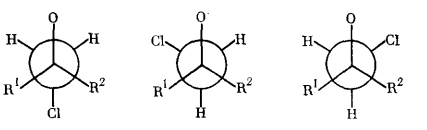
The phosphoryl compounds with a single halogen or cyanoalkyl group attached to the phosphorus atom can be regarded as more complex than compounds (I)–(VIII). Apart from the steric interactions, additional intramolecular effects may be manifested in derivatives of this series.

Fairly detailed spectroscopic studies have been made for the compounds $Cl_2P(O)CH_2Cl$ (IX)[40,41], $Cl_2P(S)CH_2Cl$ (X)[40,42], $F_2P(O)CH_2Cl$ (XI), $F_2P(S)CH_2Cl$ (XII), and $Cl_2P(O)CH_2CH_2Cl$ (XIII)[24].

The number of observed absorption bands in the infrared spectra and lines in the Raman spectra of compound (IX) in the liquid state is greater than 18, which is inconsistent with the concept of a conformationally rigid eight-atom non-linear molecule. Comparison of the spectra of liquid and solid specimens of compound (IX) revealed a tendency towards a simplification of certain parts of the spectrum on crystallisation, which also indicates the existence of a mixture of conformers in the liquid phase. An analogous picture has been observed also for compounds (X)–(XIII). It has been established by the dipole moment and Kerr effect methods that, in a non-polar medium, there is equilibrium between the *trans*-conformer (80%) and the *gauche*-conformer of compound (XI)[43]. Certain considerations concerning the structures of the conformers produced in a given series of compounds have been put forward[24,40]. Special conformational studies on compounds of the type $R_1R_2P(O)CH_2Cl$ undertaken to discover the influence of the nature of the substituents R_1 and R_2 on the hindered internal rotation about the $P-C_{sp^3}$ bond have been made by infrared spectroscopic and dipole moment methods[44], Raman spectroscopy, differential thermal analysis[45], and ^1H NMR.[46] Compounds with $R^1 = R^2 = Cl$ (IX), $R^1 = R^2 = CH_3$ (XIV), $R^1 = Cl$ and $R^2 = CH_3$ (XV), $R^1 = R^2 = C_6H_5$ (XVI), $R^1 = C_6H_5$ and $R^2 = Cl$ (XVII), and $R^1 = C_6H_5$ and $R^2 = CH_3$ (XVIII) were investigated.

The joint examination of Raman spectroscopic and differential thermal analysis data yielded additional evidence for the conformational inhomogeneity of compounds (XV) and (XVII) in different phase states. The joint analysis of the vibrational and ^1H NMR spectra made it possible to explain the changes in the geminal constants for the interaction of the phosphorus and proton nuclei in media of different polarity and to estimate the parameters for individual conformers. The results of an electron diffraction study of compound (IX)[47] are comparable with those obtained elsewhere[44–46].

The possibility of the existence of three conformers or their equilibria was examined for compounds (IX) and (XIV)–(XVIII):



The equilibrium between several conformers has been observed in a non-polar medium for all the compounds (Table 1)[44].

Table 1. The percentages of conformers in solutions of compounds (IX) and (XIV)–(XVIII) in CCl_4 at 298 K[44].

No.	Compound	*trans*-Conformer	*gauche*-1-Conformer	*gauche*-2-Conformer
(IX)	$Cl_2P(O)CH_2Cl$	60	20	20
(XIV)	$(CH_3)_2P(O)CH_2Cl$	90	5	5
(XV)	$Cl(CH_3)P(O)CH_2Cl$	60	10	30
(XVI)	$(C_6H_5)_2P(O)CH_2Cl$	10	45	45
(XVII)	$Cl(C_6H_5)P(O)CH_2Cl$	30	10	60
(XVIII)	$C_6H_5(CH_3)P(O)CH_2Cl$	30	35	35

The influence of the nature of the substituents at the phosphorus atom on the relative stabilisation of the conformers involved in the equilibria has been elucidated on the basis of conformational analysis: when the chlorine atoms in compound (IX) are replaced by methyl groups as in compound (XIV), the equilibrium shifts significantly towards the *trans*-form. Calculation of the energies of the steric and electrostatic interactions of the non-bonded atoms showed[44] that steric factors do not play a significant role in the displacement of the equilibrium for compound (IX) and that the greater stability of the *trans*-form is due to the mutual repulsion of the C–Cl dipole and the most polar P=O group. The role of steric interactions in compound (XIV) increases (there is some stabilisation of the *gauche*-form), but the interaction of the dipoles remains the decisive factor.

Analogously allowance for the steric and dipole–dipole interactions in compound (XV) permitted an explanation of the existing conformational equilibrium with satisfactory accuracy. As in compounds (IX) and (XIV), the electrostatic interaction plays the main role in compound (XV). Even for the two *gauche*-conformers, where the orientations of the C–Cl bond and of the P=O bond, which is the most polar of the bonds involving the phosphorus atom, are the same, the energy difference is wholly determined by the polar interactions involving the P–C and P–Cl dipoles which are weaker but their orientations are opposed.

When the methyl groups are replaced by phenyl groups [compounds (XVI)–(XVIII)]. the relative stabilities of the conformers change and the *gauche*-conformer predominates. This can be explained by the steric hindrance due to the aromatic rings. The *trans*-orientation of the chlorine atom is unfavourable even in the presence of only one phenyl group. There is an approximately 30% content of the *trans*-conformer of compound (III), while the proportion of the corresponding conformer of the methyl analogue (XV) is 60%.

An analogous investigation of thiophosphoryl derivatives has been carried out[48]. The infrared spectroscopic and dipole moment data and conformational calculations on compounds having the general formula $R^1R^2P(S)CH_2Cl$, where $R^1 = R^2 = Cl$ (X), $R^1 = Cl$ and $R^2 = C_2H_5$ (XIX), $R^1 = Cl$ and $R^2 = C_6H_5$ (XX), and $R^1 = Cl$ and $R^2 = p\text{-}ClC_6H_4$ (XXI), indicate the existence of conformational equilibrium. The content of the less polar *trans*-form is 80% for compound (XIX) and 40% for compounds (XX) and (XXI). As for the phosphoryl derivatives the *gauche*-conformers are not identical. Comparison of the experimental dipole moments of compounds (XIX)–(XXI) and the corresponding dipole moments calculated within the framework of Exner's method[49] permitted the conclusion that the *gauche*-1 form is involved in the equilibrium, i.e., of the two possible *gauche*-forms, that in which the C–Cl bond is in the *trans*-position relative to the most bulky substituent at the phosphorus atom is actually produced.

Thus the replacement of the phosphoryl oxygen by a sulphur atom hardly leads to any serious changes in the intramolecular interactions.

The energy of rotation about the $P-C_{sp^3}$ bond can change when the substituents are varied not only at the phosphorus atom but also at the carbon atom, as already noted for alkylphosphonic acid dichlorides examined in the previous section.

A series of recent publications describe a detailed conformational analysis of dichloromethylphosphonic acid dichloride $Cl_2P(O)CHCl_2$ (XXII)[50], dichloromethylphosphonothioic acid dichloride $Cl_2P(S)CHCl_2$ (XXIII)[51], the dichloride of α-chloroethylphosphonic acid $Cl_2P(O)CH(CH_3)Cl$ (XXIV)[52], and the dichloride of α-chloroethylphosphonothioic acid $Cl_2P(S).CH(CH_3)Cl$ (XXV)[53] by means of a combined application of infrared, Raman, and NMR spectroscopic, dipole moment, and Kerr effect methods as well as theoretical conformational calculations.

The effectiveness of the vibrational spectroscopic method in the estimation of the conformational inhomogeneity of the specimens has been clearly demonstrated[51] in relation to the vibrational spectra of compound (XXIII) in the liquid and crystalline states: conformational pair equilibrium is manifested by the doublet structures of seven pairs of bands and lines due to the stretching and deformation vibrations of the P–Cl, P=S, C–Cl, P–C, and C–H bonds (Table 2).

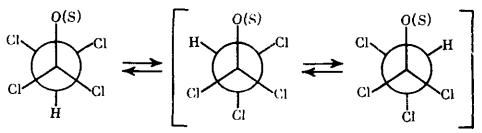
Table 2. Vibrational spectra of the compound $Cl_2P(S)CHCl_2$ (XXIII) (ν, cm^{-1})[51].

Raman spectra		I.r. spectra (liquid)	Assignment	Symmetry of isomer
liquid	crystal			
135 *dp*	135	—	—	—
190 *dp*	195	—	—	—
227 *dp*	227	—	—	—
270 *dp*	275	—	—	—
285 *dp*	285	—	—	—
365 *p*	365	—	—	—
475 *p*	473	463 m.	$\nu_s(PCl_2)$	C_1
485 *p*	—	483 m.	$\nu_s(PCl_2)$	C_s
540 *dp*	—	540 s.	$\nu_{as}(PCl_2)$	C_s
555	555	555 sh.	$\nu_{as}(PCl_2)$	C_1
625 *p*	—	624 m.	ν (P=S)	C_s
655 *p*	655	649 m.	ν (P=S)	C_1
730	727	725 sh.	ν_s (C–Cl)	C_1
740 *dp*	—	737 s.	ν_s (C–Cl)	C_s
775 *dp*	775	772 s.	ν_{as} (C–Cl)	—
810 *dp*	807	805 sh.	ν (P–C)	C_1
825	—	820 w.	ν (P–C)	C_s
1185	—	1185 v.w.	ρ (C–H)	—
1195	—	1195 v.w.	ρ (C–H)	—
2945	—	2945 w.	ν (C–H)	—
2955	—	2955 w.	ν (C–H)	—

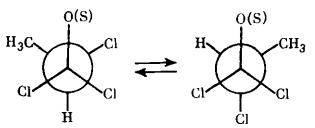
Note: *dp* = depolarised lines; *p* = polarised lines; band intensities: s. = intense (strong); m. = moderate; w. = weak; v.w. = very weak; sh. = shoulder.

It must also be emphasised that the "combined application of methods" is understood as the joint processing of information obtained independently by different physical methods using either analytical or graphical procedures. This principle was first proposed by Exner and Jehlicka[49] and Altona

et al.[54] and was subsequently developed by Vereshchagin and co-workers[55,56]. Thus graphical analysis of the squares of the dipole moments and Kerr constants (Fig. 1*a*), the squares of the dipole moments and the spin–spin coupling constants (Fig. 1*b*), and the Kerr and spin–spin coupling constants (Fig. 1*c*), and finally the joint analysis of all the three physicochemical characteristics indicated (Fig. 1*d*) led to an unambiguous identification of the conformational state of compound (XXIV)[56]. The following conformational pair equilibria have been observed for compounds (XXII)–(XXV) in a non-polar medium (dilute solutions in CCl_4):



(XXII) and (XXIII)



(XXIV) and (XXV).

As in the systems examined previously, the steric structures formed are influenced by two intramolecular effects: the steric and electrostatic interactions of the substituents at the phosphorus–carbon bond. However, allowance for only these effects in compounds (XXII) and (XXIV) is insufficient to account for the observed picture. Comparison of quantitative data on the thermodynamic parameters of the conformational equilibria of compounds (III), (IV), and (XXII) (Table 3) can be of definite assistance in this instance. In the absence of specific intramolecular interactions, the difference between the entropies of the conformers usually corresponds to their statistical weighting factors within the limits of the error of the measurements (~ 0.5 cal mol^{-1} K^{-1}), which has in fact been observed for compounds (III) and (IV), in the molecules of which there are no electronegative substituents at the α-carbon atom. The replacement of the hydrogen atoms of the alkyl fragment by chlorine atoms leads to a significant deviation from this relation. This is also accompanied by the stabilisation of the conformers with the C_1 symmetry. These changes can be explained by the formation of a weak intramolecular hydrogen bond. Its existence in one of the conformers of compound (XXII) has been demonstrated by an estimate[50] of the ratio of the absolute integral ν_{CH} band intensities due to different conformers. Thus, in the presence of protons, which have appreciable electron-accepting properties, at the α-carbon atom, the intramolecular hydrogen bond can influence the hindered internal rotation about the phosphorus–carbon bond.

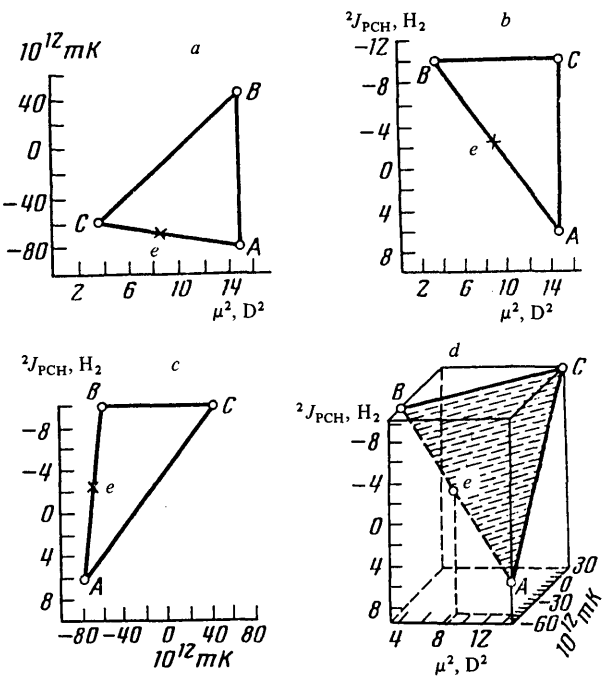


Figure 1. Graphical comparison of the squares of the dipole moments μ^2, the spin–spin coupling constants $^2J_{PCH}$, and the Kerr constants *mK* for the possible conformations of the compound $Cl_2P(O)CH(CH_3)Cl$ (XXIV): *a*) graphical comparison of μ^2 and *mK*; *b*) graphical comparison of μ^2 and $^2J_{PCH}$; *c*) graphical comparison of *mK* and $^2J_{PCH}$; *d*) graphical comparison of μ^2, *mK*, and $^2J_{PCH}$; *e*) experimental points[52].

Table 3. Thermodynamic parameters of the conformational equilibria in solutions of a number of compounds in CCl_4 at 298 K[57].

No.	Compound	$\Delta H_{C_1-C_S}$, kcal mol^{-1}	$\Delta S^{exp}_{C_1-C_S}$, cal mol^{-1} K^{-1}	$\Delta S^{theor}_{C_1-C_S}$, cal mol^{-1} K^{-1}	$\Delta\Delta S$, cal mol^{-1} K^{-1}
(III)	$Cl_2P(O)CH_2CH_3$	0.00	1.65	1.40	−0.25
(IV)	$Cl_2P(O)CH(CH_3)_2$	0.50	1.00	1.40	0.40
(XXII)	$Cl_2P(O)CHCl_2$	−1.32	−2.30	1.40	3.70
(XXIII)	$Cl_2P(O)CH(CH_3)Cl$	−1.00	−2.50	0.00	2.50
(XXV)	$Cl_2P(S)CH(CH_3)Cl$	0.10	1.30	1.40	0.10

Note: $\Delta H_{C_1-C_S}$ and $\Delta S_{C_1-C_S}$ are the differences between the enthalpies and entropies respectively; $\Delta\Delta S$ are the differences between the experimental entropies and the entropies calculated from the statistical weights of the conformers.

The hindered internal rotation in a compound with a single bromomethyl group at the phosphorus atom has been investigated in relation to the dibromide of bromomethylphosphonic acid $Br_2P(O)CH_2Br$ (XXVI)[41]. The authors[41] suggested that the bands in the infrared spectra of these compounds, whose intensity increases with decrease of temperature, are associated with the conformer having a plane of symmetry (i.e. a *trans*-disposition of the P=O and C–Br bonds). However, this initial hypothesis cannot be regarded as correct. Comparison of the spectra of compounds (IX) and (XXVI)[57] showed that the replacement of substituents [in the given case of chlorine atoms at the phosphorus atom and in the chloromethyl group of compound (IX) by bromine atoms, as in compound (XXVI)] can entail a redistribution of the contributions of different intramolecular interactions. Therefore, in some cases the *trans*-conformation can be stable, while in others the *gauche*-conformation is stable.

The incorrect hypothesis put forward by Nyquist[41] led to his assignment of the high-frequency component of the doublet ν(P=O) band in the spectrum of compound (IX) to the conformer with the C_1(*gauche*) symmetry and of the corresponding component in the spectrum of compound (XXVI) to the conformer with the C_s(*trans*) symmetry. Spectroscopic studies of a large series of phosphoryl compounds have shown[44] that the high-frequency component of the ν(P=O) vibration corresponds to the more polar conformer in the given series. It is therefore more logical to assume that the high-frequency component of the ν(P=O) band in the spectrum of compound (XXVI) corresponds to the *gauche*-isomer. Comparison of the spectra of compounds (IX) and (XXVI), obtained under identical conditions, reveals a redistribution of the intensities of the ν(P=O) and $\nu_{as}(PX_2)$ bands on passing from the chloromethyl to the bromomethyl derivative. This is apparently due to the displacement of the conformational equilibrium and not to a change in the ratio of the absolute integral intensities, since a parallel behaviour of absorption bands of different types has been observed. Temperature measurements have shown that, with decrease of temperature, the intensities of the low-frequency component of the ν(P=O) band in the spectrum of compound (IX) and of the high-frequency component in the spectrum of compound (XXVI) increase.

Thus a greater stability of the *trans*-conformer is characteristic of the dichloride of chloromethylphosphonic acid in a non-polar medium, while the *gauche*-conformer of the dibromide of bromomethylphosphonic acid is the more stable, which can also be explained primarily by the intensification of the influence of steric interactions on the energetic stabilities of the conformers. The significant increase in the bulk of the substituents at the phosphorus atom and in the halogenomethyl group led to an increase of the energy of the molecule in the *trans*-conformation (the bromine atom of the bromomethyl group is located in the projection between the two bulky bromine atoms) compared with the *gauche*-conformation (the bromine atom of the bromomethyl group is located between the bromine atom and the small oxygen atom).

The conformations of bromomethyldimethylphosphine oxide $(CH_3)_2P(O)CH_2Br$ (XXVII) and iodomethyldimethylphosphine oxide $(CH_3)_2P(O)CH_2I$ (XXVIII) have been investigated[58,59] by infrared and ^1H NMR spectroscopy and the dipole moment and Kerr effect methods. The agreement between the estimates of the conformational composition obtained by each of the above physical methods is to within 5%. It has been established that the *trans*-conformation predominates in compounds (XXVII) and (XXVIII) in a non-polar medium. This emphasises the decisive role of the electrostatic interaction of the polar group (namely P—O and C—Hal).

The steric structures of phosphoryl compounds with cyanomethyl groups, namely cyanomethyldiethylphosphine oxide $(C_2H_5)_2P(O)CH_2CN$ (XXIX) and cyanomethyldiphenylphosphine oxide $(C_6H_5)_2P(O)CH_2CN$ (XXX), have been investigated by the dipole moment and infrared spectroscopic methods[60,61]. The ratio of the *trans*- and *gauche*-conformers (0.8:0.2) of compound (XXIX) proved similar to the experimental ratio determined under the same conditions for compound (IX). The estimation of the contributions of the intramolecular effect showed that the repulsion of the dipoles leads to a relative energy gain for the *trans*-conformer by 1.3 kcal mol^{-1}. The equilibrium position for compound (XXX) is also somewhat displaced towards the *trans*-form. Comparison of the proportions of the conformers of compounds (XIV) and (XVI) (Table 1), on the one hand, and compounds (XXIX) and (XXX), on the other, has shown that for the latter pair of compounds the bulk of the substituents at the phosphorus atom no longer plays a significant role. The dipole–dipole interactions (the differences between the interaction energies of the dipoles of the *gauche*- and *trans*-conformers calculated theoretically virtually agree with the experimental values) have a greater influence in this case. Even a small decrease in the bulk of the substituents at the α-carbon atom probably weakens appreciably the steric interactions with the substituents at the phosphorus atom. The experimental difference between the free energies for compound (XXIX) is greater by 0.2 kcal mol^{-1} than for compound (XXX). The electrostatic interaction energies for these compounds differ similarly.

Thus the electrostatic factor can explain not only the observed ratio of the conformers but also the influence of the nature of the substituents at the phosphorus atom on the position of the conformational equilibrium.

Summarising the data discussed above concerning the hindered internal rotation about a single P—C_{sp^3} bond, the following observations may be made. Despite the availability of only a small amount of direct reliable quantitative data for the magnitudes of the potential barriers, detailed conformational studies of the series of compounds (I)–(XXX) which we selected suggest that the hindered internal rotation about the given bond obeys all the rules known for non-conjugated compounds and can be described satisfactorily with the aid of simple models[62,63]. This conclusion is confirmed by the results of calculations on steric and electrostatic interactions mentioned above. A distinctive feature of the group of compounds considered is the presence of the polar P=O bond, which can exert a significant influence on the orientation of the polar substituents at the α-carbon atom.

III. HINDERED INTERNAL ROTATION ABOUT A P—C_{sp^2} BOND

1. Derivatives of Vinylphosphonic Acid

The dichloride $Cl_2P(O)CH=CH_2$ (XXXI) can be regarded as the simplest derivative of vinylphosphonic acid. Its vibrational spectra in the gaseous, liquid, and crystalline states and in solutions of different polarity have been discussed[64]. The infrared spectra of the liquid compound (XXXI) and of its solutions show a doublet ν(C=C) band. The ratio of the intensities of the components of this doublet varies with the polarity of the medium and temperature. The spectrum simplifies on crystallisation: only the high-frequency component of the ν(C=C) band remains and the band at 485 cm^{-1}, which has not been assigned to a specific type of vibrations, disappears. All these factors enabled the authors[64] to postulate that the existence of two conformers is characteristic of the liquid state and solutions of compound (XXXI): the *S-cis*- and *S-trans*-conformers, analogously to the esters of acetyl- and benzoyl-phosphonic acids, vinylphosphonates, and vinylphosphine oxides whose conformations had been investigated previously by the dipole moment method[65,66]. Remizov et al.[64] also present data for the difference between the internal energies (0.6 kcal mol^{-1}) and the potential barrier (4.0–5.0 kcal mol^{-1}), which can be regarded as approximate in view of the narrow experimental temperature range and the uncertainty of the approximations used in the calculation of the heights of the barriers, which was already mentioned above.

Another paper[67] presents data obtained in an electron diffraction study of compound (XXXI). Comparison of the geometrical parameters of the molecules of compounds (XXXI) and (I) reveals insignificant differences between the corresponding bond lengths and in the valence angles. The bond lengths in compounds (I) and (XXXI) are respectively as

follows (Å): l_{P-C} = 1.800 ± 0.025 and 1.817 ± 0.033, l_{P-Cl} = 2.032 ± 0.009 and 2.016 ± 0.004, and $l_{P=O}$ = 1.448 ± 0.005 and 1.455 ± 0.011, while the valence angles in compound (XXXI) are ∠O=P—Cl = 116.8° ± 1.5°, ∠O=P—C = 119.5° ± 3.3°, and ∠Cl—P—Cl = 101.6° ± 1.2°. Electron diffraction studies[67] established that the *cis*-conformer predominates in the gas phase. Taking into account the data of Remizov et al.,[64] Naumov and Shaidullin[67] refined the geometrical parameters of the molecule for 10, 20, and 30% of the *trans*-conformer (assuming that the bond lengths and valence angles are the same in both conformations). The best agreement with experiment was achieved for the equilibrium with a 20% content of the *trans*-conformer. The revised bond lengths and valence angles thus obtained differ only slightly from those indicated above. The characteristic feature discovered in this system is that the O=P and C=C bonds in the dominant *cis*-conformation are not located in a single plane; the dihedral angle between them is 12°.

The photoelectron spectrum of vinylphosphonic acid dichloride (XXXI) has been investigated and calculated by the CNDO/2 method[68,69]. According to the calculations, the dependence of the total energy of the molecule of compound (XXXI) on the dihedral O=P—C=C angle has an absolute minimum for the *cis*-orientation of the P=O and C=C bonds and a relative minimum for the *trans*-orientation. The total energy minimum in the case of the *cis*-conformation is due to the non-valence interactions, while the minimum in the case of the *trans*-conformation arises as a consequence of the electrostatic interactions of the polar group, which are related to the effective charges on the corresponding atoms. The infrared spectra quoted by Zverev et al.[69] (see also Remizov et al.[64]) showed signs of a conformational equilibrium for compounds in the liquid state and in solutions and the stabilisation of one of the structures in the gas phase. According to Zverev et al.,[69] the photoelectron spectra make it possible to interpret, to a first approximation, the experimental ionisation potentials as the ionisation energies of the orbitals of individual fragments. The high π(C=C) ionisation potential for compound (XXXI) can be explained by the inductive effect and not the specific manifestation of the π—π interaction.

The study of vinylphosphonic acid difluoride $F_2P(O)CH=CH_2$ (XXXII) by electrical methods showed[43] that equilibrium between the *cis*- and *trans*-conformers, with an appreciable predominance (70%) of the former, is characteristic of compound (XXXII) in a non-polar medium, i.e. the replacement of Cl atoms by F atoms has an insignificant influence on the conformational equilibrium.

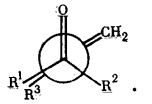
According to Remizov et al.,[64] the replacement of the hydrogen atom at the α-carbon atom in compound (XXXI) by a methyl group as in the compound $Cl_2P(O)C(CH_3)=CH_2$ (XXXIII) or of the phosphoryl oxygen atom by a sulphur atom to give the compound $Cl_2P(S)CH=CH_2$ (XXXIV) influences significantly the hindered internal rotation about the $P-C_{sp^2}$ bond. No signs of conformational equilibrium were observed in the infrared spectra of these compounds. The stabilisation of a single structure of compound (XXXIV) can be explained, according to Remizov et al.,[64] by the fact that the replacement of the phosphoryl oxygen atom by a sulphur atom should entail a significant decrease of the P=X bond order as a result of the weaker π-bonding between the *p* orbital of the sulphur atom and the vacant 3*d* orbitals of the phosphorus atom. Consequently a higher electron density deficiency should be obtained at the phosphorus atom with increase of the P—C bond order. In order to explain the observed phenomenon, it is evidently also necessary to take into account the steric effects, since the steric factor should influence the conformational equilibrium following the replacement of the oxygen atom of the phosphoryl group by a sulphur atom or of the hydrogen at the α-carbon atom by a CH_3 group.

Substituted styrylphosphonates have been investigated by NMR using lanthanide shift reagents[70]: $Cl_2P(O)CH=CH(C_6H_5)$-*trans* (XXXV), $Cl_2P(O)CH=C(CH_3)C_6H_5$-*trans* (XXXVI), $Cl_2P(O)CH=CH(C_6H_5)$-*cis* (XXXVII), $Cl_2P(O)CH=C(Cl)C_6H_5$-*trans* (XXXVIII), and $(CH_3)_2P(O)CH=CH=CH(C_6H_5)$-*trans* (XXXIX). According to Berkova et al.,[70] in solutions of compounds (XXXV), (XXXVI), and (XXXIX) in carbon tetrachloride there is an equilibrium between the *S-cis*- and *S-trans*-conformers, while the stabilisation of the *S-trans*-conformer is characteristic of compounds (XXXVII) and (XXXVIII). On the other hand, under identical experimental conditions, it has been assumed that the *S-trans*- and *S-cis*-structures predominate for compounds (XXXV) and (XXXIX) respectively, which is due to the influence of the nature of the substituent at the phosphorus atom on the hindered internal rotation about the $P-C_{sp^2}$ bond.

In order to solve the problem of the conformational equilibria in complex compounds such as (XXXV)—(XXXIX), it would be desirable to apply also the vibrational spectroscopic method. It is then essential to carry out a series of spectroscopic studies in order to assign reliably the set of bands in the infrared spectra or lines in the Raman spectra to rotational isomers, because the existence of a complex pattern in any one part of the spectrum does not alone constitute a confirmation of the existence of conformational equilibrium. Thus, in the study of the Raman spectra of the compounds $ROCH=\underset{\displaystyle Cl_2\overset{|}{P}(O)}{C}-CCl=CH_2$ (XL), Batuev et al. [71] noted a splitting of the ν(P=O) band into four components, and, without quoting any additional evidence, they assigned each component to a particular conformer; such interpretation of the spectra cannot be regarded as well founded.

Patanovskii et al.[43] investigated the compound $F_2P(O)CH=CH(C_6H_5)$ (XLI) by the dipole moment and Kerr effect methods. The experimental data obtained agree with the hypothesis of equilibrium between the *S-cis*-conformer (10%) and the *S-trans*-conformer (90%).

Data obtained as a result of the investigation of the steric structures of a small series of compounds (XXXI)—(XLI) provide only initial ideas concerning the character of the rotation about a single $P-C_{sp^2}$ bond. In order to reach specific conclusions, it is necessary to obtain additional data for a large number of phosphoryl compounds with a single vinyl group and a wide variety of other substituents at the phosphorus atom. Nevertheless, within the framework of the concept of conformational energy as the sum of the contributions by the simplest intramolecular effects, it is already possible to postulate that the role of the steric non-valence interactions in the stabilisation of the conformers as the molecules of the compounds investigated is decisive. The absence of appreciably skewed forms in the series of derivatives with the vinyl bond, in contrast to the alkylphosphonic acids (I)—(XXX) for which these forms are energetically stable, can apparently be explained by the geometry of the bonds involving the α-carbon atom. The sp^2-hybridisation of the orbitals of the α-carbon atom in compounds (XXXI)—(XLI) is responsible for the disposition of all three bonds in a single plane. In the skewed conformation with the dihedral angle φ(O=P—C=C) = 60° the third bond associated with the α-carbon atom therefore eclipses one of the substituents at the phosphorus atom:



This apparently results in the loss of the energy of the steric interaction compared with the *S-cis*- and *S-trans*-conformations in which the CH_2 group or the substituent R^3 accepts the phosphoryl oxygen atom whose steric repulsion energy is minimal.

2. Derivatives With a Single Aryl Substituent at the Phosphorus Atom

The geometrical parameters of the molecule of phenylphosphonic acid dichloride $Cl_2P(O)C_6H_5$ (XLII) are fairly close to those of compound (XXXI)[72]. Only some shortening of the $P-C_{sp^2}$ bond in the phenol derivative (l = 1.76 Å) compared with the vinyl derivative (l = 1.82 Å) should be noted. The conformation in which the phosphoryl bond and the benzene ring are located in a single plane has been assigned to compound (XLII) in the gas phase. The steric interactions between the non-bonded atoms have been analysed[72] in terms of the scheme developed by Magnasco[73]; the analysis showed that this type of interaction together with conjugation can influence the stability of the structure presented above. The spectroscopic study of compounds (XLII) and $Cl_2P(S)C_6H_5$ (XLIII) demonstrated, according to Remizov and Kuramshi[74], the existence of only one isomer in the liquid phase.

Certain derivatives of arylphosphine oxides have been investigated by the dipole moment and Kerr effect methods. Data have been obtained for solutions in carbon tetrachloride of the oxides of dimethyl-*p*-tolylphosphine $(CH_3)_2P(O)(p\text{-}CH_3).C_6H_4$ (XLIV), di-t-butyl-*p*-tolylphosphine $(t\text{-}C_4H_9)_2P(O).(p\text{-}CH_3)C_6H_4$ (XLV), and *p*-cyanophenyldimethylphosphine $(CH_3)_2P(O)(p\text{-}CN)C_6H_4$ (XLVI)[75], as well as the oxides of dimethylphenylphosphine $(CH_3)_2P(O)C_6H_5$ (XLVII), *p*-chlorophenyldimethylphosphine $(CH_3)_2P(O)(p\text{-}Cl)C_6H_4$ (XLVIII), and *m*-chlorophenyldimethylphosphine $(CH_3)_2P(O)(m\text{-}Cl)C_6H_4$ (XLIX).[76] However, the conclusions of various investigators concerning the orientation of the benzene ring in compounds (XLIV)–(XLIX) do not entirely agree. Thus alternative structures have been proposed for compound (XLIV): the bisector structure[75] and the conformation in which the angle between the $C_{sp^2}-P=O$ plane and the plane of the benzene ring is 46°.[76] This discrepancy between the conclusions reached in the two investigations[75,76] cannot be explained solely by the discrepancy between the experimental molar Kerr constants. Evidently, the differences between the initial parameters used by the authors to calculate the anisotropy of the polarisability can also be a cause.

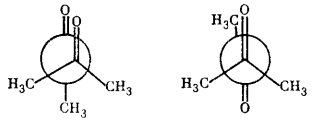
Since there are at present no rigorous criteria for the selection of the electro-optical parameters within the framework of an additive scheme, theoretical conformational calculations have been carried out in terms of the atom–atom approximation[77]. The energies of the non-valence interactions have been calculated for different conformations of the oxides of ethylphenylphosphine $C_2H_5(H)P(O)C_6H_5$ (L), diethylphenylphosphine $(C_2H_5)_2P(O)C_6H_5$ (LI), and di-t-butylphenylphosphine $(t\text{-}C_4H_9)_2P(O)C_6H_5$ (LII), in addition to compounds (XLII) and (XLVII). The results of the calculation showed that, in the presence of symmetrical substituents, the bisector orientation of the benzene ring is the most favourable from the standpoint of non-valence interactions. The barrier to internal rotation increases with the bulk of the substituents. It is noteworthy that the form of the calculated potential curves permits the possibility of torsional vibrations of the benzene ring relative to the P–C bond with an amplitude of ±15°.

When the methyl groups of one of the ethyl substituents in compounds (XL) and (LI) are in the *trans*-positions relative to the P=O bond, the benzene ring deviates from its bisector position towards one in which it eclipses the P–H bonds in the molecules of compound of (L) or one in which it eclipses the substituent with the *gauche*-conformation of the methyl group in compound (LI). Since there is no such possibility for compound (LII), it assumes a stable bisector conformation requiring considerable deformations of the valence angles at the phosphorus atom to the tetrahedral values. In the presence of identical substituents at the phosphorus atom, the benzene ring probably tends to assume the bisector position. Attention should also be drawn to the considerable similarity between the steric structures of phosphoryl compounds with vinyl and phenyl groups. The *S-cis*- and *S-trans*-conformations or their equilibrium mixture are characteristic of the first group. The bisector conformation of the benzene ring can be regarded as the *S-cis,trans*-form. Evidently, the non-valence steric interactions are decisive factors for the stabilisation of such orientation of the vinyl and phenyl groups. In agreement with Bochvar et al.,[78] no evidence has been found for the influence of conjugation of the $\pi-\pi$ or $p\pi-d\pi$ type on the stereochemistry of these molecules.

3. Derivatives with a Carbonyl Group at the Phosphorus Atom

Compounds containing the P(O)–C(O) fragment are convenient objects for investigation from the standpoint of vibrational spectroscopic and dipole moment methods in view of the presence of two polar bonds (phosphoryl and carbonyl). However, in the vast majority of cases the molecules investigated contain stereochemically irregular substituents at the phosphorus and carbon atoms and in a rigorous study must be treated as systems with several different axes of rotation. Only two compounds having fixed dispositions in space of the groups adjoining phosphorus and carbon have so far been investigated: the compounds $(CH_3)_2P(O)C(O)CH_3$ (LIII) and $[(CH_3)_3C]_2P(O)C(O)C(CH_3)_3$ (LIV).

Compound (LIII) has been studied by Kostyanovskii et al.,[79,80] by infrared and ^1H NMR spectroscopic methods. The infrared spectra of the liquid compound (LIII) have been found to contain two bands, assigned to $\nu(C=O)$ vibrations, with maxima at 1723 and 1760 cm^{-1}. Apart from the equilibrium between two conformers, the authors of these studies discussed also other possible causes of the appearance of doublet absorption bands in the range 1700–1800 cm^{-1}. In particular the hypothesis of the occurrence of the Fermi resonance of the vibrations in the given range was considered and ruled out, since both bands remained intense in different solutions. The ^1H NMR data also agree with the hypothesis of equilibrium between two conformers. Structures with the *cis*- and *trans*-disposition of the P=O and C=O bonds were proposed as the possible conformers.



Laskorin et al.[81] noted a unique and symmetrical character of the absorption in the spectrum of compound (LIII) at the $\nu(C=O)$ frequency and, although they do not discuss a specific structure of compound (LIII), comparison of the results of the above investigations[79–81] throws doubt on the initial conclusion concerning the conformational equilibrium.

A subsequent study by Laskorin et al.[82] was undertaken to solve the problem of the possible steric structure of ketophosphoryl derivatives. Only one $\nu(C=O)$ band was

observed in the infrared spectra of the compounds, including (LIV). Considering the possibility of the existence of compound (LIV) as the *cis*-, *trans*-, and *gauche*-isomers, the authors[82] assumed that the *trans*-conformation is the most probable having resorted to the Stuart–Briegleb model. The inadequate information about the structure of the group of compounds considered so far precludes a conclusion concerning the specific features of the steric orientation of the P=O and C=O bonds in the absence of internal rotation of other fragments.

IV. THE STERIC STRUCTURES OF COMPOUNDS WITH TWO AND THREE IDENTICAL IRREGULAR FRAGMENTS

1. Derivatives with Alkyl Groups

It is evident from the data described above (Section II) that a skewed position relative to the bonds adjoining the phosphorus atom is characteristic of alkyl fragments. There exist three such positions for each alkyl group. The number of possible different steric structures in the case of two and three alkyl fragments therefore increases as a result of internal rotation about the P–C_{sp^3} bonds, which leads to additional problems in the conformational analysis of such systems. X-Ray diffraction data for the compounds $(C_2H_5)_3$.P(S) (LV) and $(C_2H_5)_3P(Se)$ (LVI) confirm that the skewed disposition of the alkyl fragment is preferred[83,84]. The vibrational spectra of such compounds in the crystalline state have been interpreted[84].

Solutions of trialkylphosphine oxides having the general formula $Alk_3P(O)$, where Alk are normal unbranched hydrocarbons in which the number of carbon atoms ranges from one as in the compound $(CH_3)_3P(O)$ (LVII) to 16 as in the compound $[(CH_3)(CH_2)_{15}]_3P(O)$ (LXXII), have been investigated[85–87].

The steric structures of the conformers of compounds (LVII)–(LXXII) have not been described accurately but the possibility of rotations about the P–C_{sp^3} and C_{sp^3}–C_{sp^3} bonds, which lead to a disposition of the alkyl fragment in the vicinity of the phosphoryl linkage, has not been ruled out.

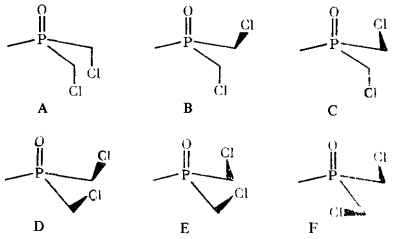
There exist definite data in the literature concerning the conformational equilibria of compounds with two alkyl groups at the phosphorus atom. Thus detailed analysis of the infrared spectra of compounds of the type $ClP(O)Alk_2$, where Alk = CH_3 [compound (LXXIII)], C_2H_5 [compound (LXXIV)], C_3H_7 [compound (LXXV)], iso-C_3H_7 [compound (LXXVI)], C_4H_9 [compound (LXXVII)], s-C_4H_9 [compound (LXXVIII)], or C_5H_{11} [compound (LXXIX)],[88] made it possible to isolate a single ν(P–Cl) band in the spectrum of compound (LXXIII) and a doublet in the spectra of compounds (LXXIV)–(LXXIX). The disappearance of one of the components of the doublet from the spectrum of the solid compound (LXXIV) and the redistribution of the band intensities in the spectra when the temperature of the liquid compounds (LXXIV)–(LXXVIII) is altered indicate the existence of a mixture of conformers; the differences between the internal energies should be of the order of magnitude of ~ 0.4 kcal mol^{-1}.

Electrical methods proved to be fairly effective in the determination of the structures of such complex systems. Thus the application of the dipole moment and Kerr constant methods to diethylpropynylphosphine oxide $(C_2H_5)_2P(O)C{\equiv}C(CH_3)$ (LXXX) showed that the C–CH_3 bonds in the ethyl groups are only in the *gauche*-positions relative to the P=O bond[89].

In view of the large number of possible conformational equilibria and the small amount of reliable data available, one cannot at present reach unambiguous conclusions concerning the conformational composition of the group of compounds considered.

2. Derivatives with Two and Three Halogenomethyl Groups

The structures of dichloromethyl(methyl)phosphine oxide $CH_3P(O)(CH_2Cl)_2$ (LXXXI) and the chloride of di(chloromethyl)phosphinothioic acid $ClP(S)(CH_2Cl)_2$ (LXXXII) have been discussed[90] on the basis of data obtained by the vibrational spectroscopic, dipole moment, and Kerr effect method. It was established that each of the C–Cl bonds in the molecules of these compounds can have the *trans*-orientation or one of the two possible *gauche*-orientations (g_1–in the direction of the methyl group, g_2–in the direction of the chloromethyl group), i.e. altogether there is a possibility of six sterically incompatible conformations:

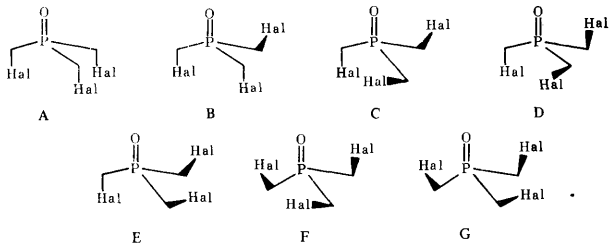


Equilibrium between two conformers, with the less polar conformer predominating (0.7:0.3), has been observed in a dilute solution of compound (LXXXI) in CCl_4. The measured dipole moments and Kerr constants led to the conclusion that the weakly polar form A and also one or several forms (B, C or D) having positive Kerr constants are involved in the equilibrium. This conclusion was confirmed by plotting the square of the dipole moment against the Kerr constant. The equilibria A ⇌ B and A ⇌ C agreed best with these spectroscopic data. The structure thus discovered proved comparable to the structure described previously for the analogue of this compound with a single chloromethyl group, i.e. the *trans*-orientation of the P=O and C–Cl bonds proved to be preferable.

Substitution of the phosphoryl oxygen atom by sulphur and of the CH_3 group by chlorine, as in compound (LXXXII), leads to a considerable stabilisation of one of the least polar forms (A or B); the fraction of the more polar structure (most probably the C structure) does not then exceed 10%.

In order to follow the variation of the steric structures of compounds when the halogen atom in the halogenomethyl group is replaced, a study was made of dibromomethyl(methyl)phosphine oxide $CH_3P(O)(CH_2Br)_2$ (LXXXIII) and di-iodomethyl(methyl)phosphine oxide $CH_3P(O)(CH_2I)_2$ (LXXXIV) by means of a combined study of the infrared, Raman, and ^1H NMR spectra, the dipole moments, and the Kerr effect[91]. It was established that substitution of chlorine atoms by bromine and iodine atoms in the halogenomethyl groups leads to a fairly appreciable alteration of the molecular structure. For compounds with two bromo- and iodo-methyl groups, the conformation with the *trans*-orientation of both C-Hal bonds is not involved in the equilibrium. The most stable proved to be the form with the *trans–gauche* disposition of the C–Hal bonds, where the halogen atoms are remote from one another, which rules out steric hindrance and, as a consequence of the electrostatic interaction, one C–Hal bond is in the *trans*-position relative to the P=O group.

Molecules in which three conformationally irregular groups are attached to the phosphorus atom are the most interesting and at the same time most complex. In the molecules of tri(halogenomethyl)phosphine oxides each C–Hal bond has either the *trans*-orientation or one of the *gauche*-orientations relative to the phosphoryl group, i.e. there is a possibility of seven conformations:



The conformational equilibrium of tri(chloromethyl)phosphine oxide $(CH_2Cl)_3P(O)$ (LXXXV) has been analysed[92]. The infrared spectra of this compound indicated equilibrium between two conformers in non-polar solutions (in proportions of 0.7:0.3), the less polar component predominating. Comparison of the experimental dipole moments and Kerr constants with the corresponding quantities evaluated by a graphical method established that all three C–Cl bonds in the dominant conformer are in the *trans*-positions relative to the P=O bond (structure A), while in the energetically less favourable conformer they are in the *gauche*-positions, all being rotated to one side (structure F). In principle, this result agrees with data obtained for phosphine oxide with one or two chloromethyl groups. It was of interest to note that the equilibrium found for tri(chloromethyl)phosphine oxide corresponds to a cooperative transition of all three chlorine atoms from the *trans,trans,trans*-positions to the *gauche,gauche,gauche*-positions.

The predominance of the B structure in the case of three bromomethyl groups was observed in an analogous study of tri(bromomethyl)phosphine oxide $(CH_2Br)_3P(O)$ (LXXXVI) and tri(iodomethyl)phosphine oxide $(CH_2I)_3P(O)$ (LXXXVII), which indicates an appreciable role of not only steric but also electrostatic interactions of the strong P=O and C–Br dipoles in the conformational equilibrium. The subsequent replacement of bromine atoms by iodine atoms led to the displacement of the conformer having the *trans,trans*-orientations of the P=O and C–Hal bonds from the equilibrium. The *gauche, gauche,gauche*-structure F was found to predominate in this case.

Thus the influence of two intramolecular effects (those of the steric and electrostatic interactions of the non-bonded atoms) on the structures of compounds with several halogenomethyl groups has been clearly followed. The equilibrium which obtains in the case of tri(chloromethyl)phosphine oxide indicates the approximately identical influence of two of the factors indicated above: the *trans,trans,trans*-structure is a result of the Coulombic repulsion of the dipoles of the P=O and C–Cl groups, while the *gauche,gauche,gauche*-structure is determined by steric interactions. Steric interactions predominate for compounds with iodomethyl groups, so that the *gauche,gauche,gauche*-disposition of the P=O and C–I bonds is observed in the preferred conformation.

3. Two and Three Vinyl or Phenyl Groups at the Phosphorus Atom

The structure of the compound $ClP(O)(CH=CH_2)_2$ (LXXXVIII) has been investigated by electron diffraction[67]. Complete agreement between the experimental and calculated data was not obtained in the above studies, but the authors concluded that the conformer in which the C=C and P=O groups have a disposition intermediate between *cis* and *gauche* (which corresponds to the model with C_S symmetry and dihedral angles close to 35°) predominates. The deviation from the rigorously eclipsed disposition of these groups may be associated with the interaction of the *p* orbitals of the vinyl groups. Evidently, the solution of the problem of the structure of compound (LXXXVIII) requires its more detailed investigation using other independent methods.

The data for the steric structures of compounds containing two and three benzene rings at the phosphorus atom can be divided into three groups: the results of X-ray diffraction analysis, the results of studies in solutions, and the results of theoretical conformational calculations.

X-Ray diffraction analysis was used to investigate diphenylphosphinic acid $(C_6H_5)_2P(O)OH$ (LXXXIX)[93,94], the diphenylphosphoryl alcohols $(C_6H_5)_2P(O)(CH_2)_3OH$ (XC)[95], $(C_6H_5)_2P(O)(CH_2)_2OH$ (XCI)[96], and $(C_6H_5)_2P(O)CH_2(o\text{-}OHC_6H_4$ (XCII)[97], triphenylphosphine oxide $(C_6H_5)_3P(O)$ (XCIII)[98–100], *p*-chlorophenyldiphenylphosphine oxide $(p\text{-}ClC_6H_4)P(O).(C_6H_5)_2$ (XCIV)[101], tri(*o*-tolyl)phosphine oxide $(o\text{-}CH_3C_6H_4)_3.P(O)$ (XCV), tri(*o*-tolyl)phosphine sulphide $(o\text{-}CH_3C_6H_4)_3.P(S)$ (XCVI)[102,103], tri(*m*-tolyl)phosphine sulphide $(m\text{-}CH_3C_6H_4)_3P(S)$ (XCVII)[103], and tri(*o*-tolyl)phosphine selenide $(o\text{-}CH_3C_6H_4)_3P(Se)$ (XCVIII)[102,103]. A disposition of the planes of the benzene rings relative to the X=P–C plane (X = O, S, or Se) skewed to different extents has been established for all the derivatives listed above, but the cause of this has not been elucidated. The results of the X-ray diffraction analysis of the two crystalline modifications of compound (XCIII) show that the polymorphic transformation involves a fairly appreciable alteration of the conformation, i.e. the crystal packing has an effect. However, the extent to which the crystal field effects are responsible for the non-equivalence of the benzene rings is difficult to determine without reliable information about the molecular structure in the liquid phase and in solutions. In virtually all the studies which have yielded data for the structures of the above compounds in solutions, it was assumed that each of the three benzene rings attached to the phosphorus atom has been rotated by the same angle[104,105]. It has been found by the dipole moment and Kerr effect methods that their angle of rotation is 60°[104] or 55°[105] for compound (XCIII) and 62° for the compound $(C_6H_5)_3P(S)$ (XCIX)[104]. Analogous results have been obtained also for several substituted triarylphosphine oxides having the general formula $(XC_6H_4)_3P(O)$, where X = *p*-Cl [compound (C)], *m*-Cl [compound (CI)], $p\text{-}CH_3$ [compound (CII)], or $m\text{-}CH_3$ [compound (CIII)][105]. However, a broadening of the signals due to the fluorine atoms in the *meta*-position has been observed in the NMR spectra of the fully fluorinated triphenylphosphine oxide[106], which disagrees with the results of Aroney et al.[104] and Bulgarevich et al.[105]

The same problems arise also in the study of compounds with two benzene rings at the phosphorus atom. According to the measurements of the dipole moments and Kerr constants for methyldiphenylphosphine oxide $(C_6H_5)_2P(O)CH_3$ (CIV)[76], the dihedral angle of the benzene rings and the P=O group is 58°. Somewhat different results have been obtained for analogous compounds in other investigations[89,107,108]. Ishmaeva et al.[107] examined two types of rotations for $(C_6H_5)_2P(O)CCl_3$ (CV), $(p\text{-}CH_3C_6H_4)_2P(O)CCl_3$ (CVI), and $(p\text{-}ClC_6H_4)_2P(O)CCl_3$ (CVII): the symmetrical rotation ($\phi_1 = -\phi_2$) and the antisymmetric rotation ($\phi_1 = \phi_2$). The dihedral angles obtained are 15°, in agreement with the symmetrical rotation. The dipole moment and Kerr constant data for the compound $(C_6H_5)_2P(O)CN$ (CVIII) indicated a

structure in which the planes of the benzene ring are almost parallel to the P=O bond[108]. Thus, according to the above workers[108], the addition of the strongly electron-accepting cyano-group to the phosphorus atom does not affect the conformational behaviour of the phenyl groups and is not manifested in the intramolecular electronic interactions involving the phosphorus atom. On the other hand, the experimental Kerr constants for the compound $(C_6H_5)_2P(O)C\equiv C-CH_3$ (CIX) agree with the conformation in which the planes of the phenyl groups are close to the arrangement in which the ethynyl group is eclipsed. In this case the authors[108] concluded that the interaction of the conjugated systems of the aromatic fragments with the triple bond is a stabilising factor.

An attempt has been made[109] to estimate the stereochemical properties of compound (CIV) and the compound $(C_6H_5)_2$.P(O)H (CX) with the aid of the relation found[110] between the ratio of the intensities of the symmetrical and asymmetric vibrations in the infrared spectra and the angle between the polarisation vectors of the out-of-plane vibrations. Relations of this kind may be useful in the study of the steric structures of complex compounds, but, so long as their universality has not been tested, they must be treated with caution.

Apart from the experimental studies on individual examples of the group of compounds considered, theoretical conformational calculations have been carried out. The calculation for compound (CIV) has been performed within the framework of the method of atom–atom potential functions and it was shown that the skewed state of the benzene rings attached to the phosphorus atom relative to the O=P–C–C plane is preferred[111].

The dependence of the conformational energy on the angles of internal rotation of the benzene rings relative to the $P-C_6H_5$ bonds has been investigated for the chloride of diphenylphosphinic acid $(C_6H_5)_2P(O)Cl$ (CXI) also within the framework of the atom–atom approach with simultaneous optimisation of the bond lengths and valence angles at the phosphorus atom[77]. The calculation showed that the two conformers for which the difference between the internal energies is 0.3 kcal mol^{-1} are the most stable in terms of the given approximation. The angles $\phi_1 = 10°$ and $\phi_2 = 76°$ were obtained for one conformer and $\phi_1 = 30°$ and $\phi_2 = 15°$ were found for the other conformer. It is noteworthy that the conformations with identical angles of rotation of the benzene rings ($\phi_1 = \phi_2$), in the range 10°–40°, have energies slightly different from those of the structures indicated above (~ 0.5 kcal mol^{-1}). The possibility therefore remains that a whole series of states obtains for the molecule of compound (CXI) with both identical and different angles of rotation of the planes of the benzene ring in the range from 10° to 40°.

On the basis of experimental data for compounds containing two or three phenyl groups at the phosphorus atom, one must conclude that it is difficult to obtain reliable results concerning the orientation of the plane of the benzene ring in such compounds when the latter are in solution. The employment of the vibrational spectroscopic method in this instance is complicated by the presence in the spectra of a large number of bands of the benzene ring. On the other hand, data obtained with the aid of electrical methods (in particular the Kerr effect methods) cannot be regarded as sufficiently accurate, despite their satisfactory sensitivity, owing to the limited amount of available information about the type of variation of the anisotropy of the polarisability of the benzene rings under the influence of electronic effects in the hindered internal rotation about the $P-C_{sp^2}$ bonds.

V. THE STERIC STRUCTURES OF COMPOUNDS WITH DIFFERENT IRREGULAR SUBSTITUENTS AT THE PHOSPHORUS ATOM

The conformational analysis of compounds with different irregular substituents at the phosphorus atom is undoubtedly even more complex than the study of compounds with identical groups. This is associated both with the removal of degeneracy, and hence the increase of the number of conformers having different properties, and with the possibility, in principle, of the stabilisation of those structures which might be disregarded in the case of derivatives with identical groups in view of their instability. The employment of any one physical method in the conformational analysis of compounds of the given series can therefore lead to erroneous conclusions.

For example, the ^{1}H NMR spectra of compounds (I) and (III)–(V), $CH_3(C_6H_5)P(O)Cl$ (CXII), $C_2H_5(C_6H_5)P(O)Cl$ (CXIII), and iso-$C_3H_7(C_6H_5)P(O)Cl$ (CXIV) have been discussed[34]. In contrast to compounds (CXII) and (CXIII), in the spectrum of compound (CXIV) a doublet is observed at the $\nu(CH_3)$ frequency. The authors[34] explained this finding by the conformational equilibrium, but the merging of the signals did not occur even following an appreciable increase of temperature. The observed spectroscopic pattern cannot apparently be explained by rotational isomerism and is in fact due to the manifestation of the magnetic non-equivalence, giving rise to spectra of type ABX and A_2X for the methyl groups of compound (CXIV), which the authors[34] failed to take into account. The same interpretation has been given[112] for the protons of the chloromethyl group in the compound $(CH_3)_2NP(O)Cl(CH_2Cl)$ (CXV).

In a stereochemical study of ketophosphonate compounds, the vibrational spectroscopic method was mainly used. It has been stated[113] that there is only a single $\nu(C=O)$ band in the spectra of compounds having the general formula $(C_2H_5O)_2P(O)C(O)(CH_2)_nCH_3$, where n = 10 [compound (CXVI)], 12 [compound (CXVII)], 14 [compound (CXVIII)] and 16 [compound (CXIX)]. Analogous conclusions were reached on the basis of the Raman spectra of the compound $(C_2H_5O)_2P(O)C(O)C_6H_5$ (CXX)[114] and the infrared spectra of the compound $(C_2H_5O)_2P(O)C(O)CH_3$ (CXXI)[115], as well as a whole group of compounds having the general formula $(R'O)_2P(O)C(O)R$, where R = CH_3 and R' = C_2H_5 [compound (CXXII)], R = C_2H_5 and R' = C_2H_5 [compound (CXXIII)], R = iso-C_3H_7 and R' = C_2H_5 [compound (CXXIV)], R = t-C_4H_9 and R' = C_2H_5 [compound (CXXV)], R = C_6H_5 and R' = C_2H_5 [compound (CXXVI)], R = C_5H_9 and R' = C_2H_5 [compound (CXXVII)], R = C_6H_{11} and R' = CH_3 [compound (CXXVIII)], R = C_6H_{11} and R' = C_2H_5 [compound (CXXIX)], and R = C_6H_{11} and R' = iso-C_3H_7 [compound (CXXX)][116]. However, two ranges of variation of $\nu(C=O)$ (1656–1666 and 1698–1700 cm^{-1}) have been indicated[117] for 33 different compounds having the general formula $R(R''O)$.P(O)C(O)R', where R = C_2H_5, C_6H_5, p-$CH_3C_6H_4$, or p-ClC_6H_4, R' = C_6H_5, CH_3, p-$CH_3C_6H_4$, or p-ClC_6H_4, and R'' = CH_3, C_2H_5, C_3H_7, or iso-C_4H_9.

Detailed infrared and ^{1}H NMR spectroscopic data for the compounds $(CH_3O)_2P(O)C(O)CH_3$ (CXXXI), $(C_2H_5O)_2P(O)$.C(O)CH_3 (CXXXII), and $(CH_3O)_2P(O)C(O)C_6H_5$ (CXXXIII) have been published[118]. The infrared spectra of compounds in different phase states, in solutions of different polarity, and at different temperatures have been obtained. The type of the band characterising the absorption by the carbonyl group has led to the conclusion that conformational pair equilibrium obtains for compounds (CXXI) and (CXXXII) and that one conformer of compound (CXXXIII) is stabilised. However, only a single $\nu(C=O)$ band has again been noted[81]

for compound (CXXXI). In a special investigation[82] it has been stated that the manifestation of the second ν(C=O) band with a maximum at 1710 cm^{-1} is apparently due to an admixture of decomposition products. In the infrared spectrum of a freshly prepared and purified specimen of compound (CXXXI), the splitting of the ν(C=O) band is not observed for a liquid film and for a solution in CCl_4, while the addition of traces of acetic acid to the specimen leads to the appearance of a second absorption band at 1710 cm^{-1}. Preference has been given[82] to the *trans*-orientation of the P=O and C=O bonds.

However, in a number of instances the high sensitivity of individual physical methods to hindered internal rotation makes it possible to obtain fairly definite results even when only one method is used to study the conformations of complex compounds. Thus the considerable polarity of the P=O and C≡N bonds makes it possible to identify their relative positions in space[61]. The dipole moment method has been used[119] to investigate the steric structures of compounds having the general formula $XC_6H_4CH{=}C(CN)P(O)OC_2H_5$, where X = H [compound (CXXXIV)], *p*-NO_2 [compound (CXXXV)], *p*-Cl [compound (CXXXVI)], *p*-OCH_3 [compound (CXXXVII)], *p*-$N(CH_3)_2$ [compound (CXXXVIII)], and *m*-NH_2 [compound (CXXXIX)]. The rigidity of the $XC_6H_4CH{=}C(CN)$ fragment made it possible to infer the orientations of the phosphoryl and vinyl bonds and hence their electronic interactions. A number of other examples of this approach to conformational studies have been described in a review[120].

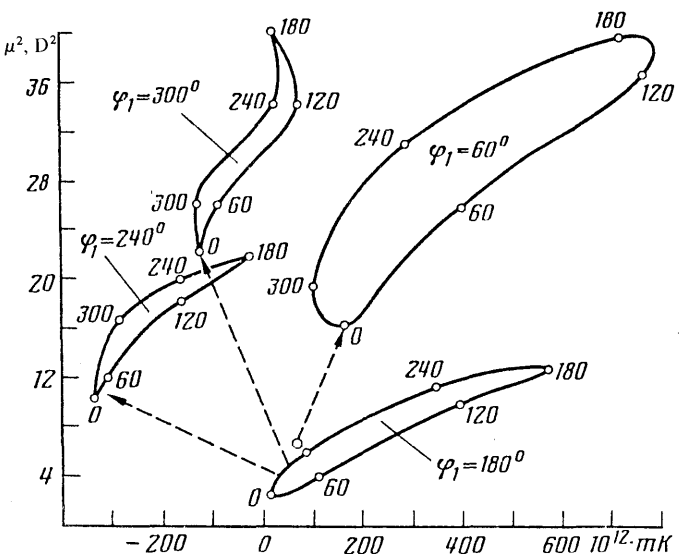
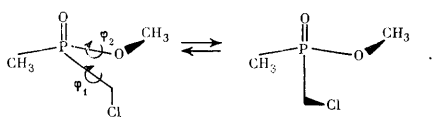


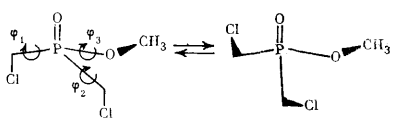
Figure 2. Graphical comparison of the dipole moments and Kerr constants for the compound $CH_3(CH_3O)P(O)CH_2Cl$ (CXL)[121].

Nevertheless, a combined physicochemical investigation is required to a greater extent than in other cases for the identification of the steric structures of organophosphorus compounds with different substituents. Such a study has been carried out of the ester of chloromethyl(methyl)phosphinic acid $CH_3(CH_3O)P(O)CH_2Cl$ (CXL)[121]. Vibrational and ^1H NMR spectroscopic data have been used in studies by the dipole moment and Kerr effect methods have been carried out. When account is taken of the possible rotations of both groups in steps of 60°, one can imagine the occurrence of 36 structures. However, all the structures in which the P=O and C—Cl, P—C and C—Cl, and P—C and O—CH_3 pairs of bonds are eclipsed can be excluded from consideration according to the data presented above in the present review and the conclusions reached by Raevskii[63]. Vibrational spectra have shown that in dilute solutions in CCl_4 compound (CXL) exists as a mixture of two conformers in which the less polar form predominates appreciably (~ 90%).

Experimental dipole moment and Kerr effect data have been assessed under the same conditions[121]. Fig. 2 compares the calculated squares of the dipole moments and Kerr constants with complete internal rotation relative to the P—O bond and four fixed positions of the P=O and C—Cl groups (the angles between the P=O and C—Cl bonds are 60°, 180°, 240°, and 300°). The experimental point is located in the vicinity of a closed curve corresponding to the set of conformations with the *trans*-orientation of the P=O and C—Cl bonds, which shows that the conformer with the *trans*-disposition of the C—Cl bond predominates in the equilibrium. The orientation of the O—CH_3 bond of this conformer can correspond to the *cis*- or *gauche*-disposition. The steric structure of the second conformer, the partner in the equilibrium in the given instance, cannot be determined with much reliability in view of its small amount. However, ^1H NMR data suggest the existence of equilibrium between the following conformers:



An analogous study has been carried out for a series of alkyl esters di(chloromethyl)phosphinic acid having the general formula $(CH_2Cl)_2P(O)OR$, where R = CH_3 [compound (CXLI)], C_2H_5 [compound (CXLII)], $CH_2CH{=}CH_2$ [compound (CXLIII)], iso-C_3H_7 [compound (CXLIV)], or C_4H_9 [compound (CXLV)].[121] The combined employment of various physical methods made it possible to identify the steric structures of these complex compounds for which the following equilibrium obtains in a non-polar medium:



Comparison of the steric structures of the series of compounds considered in this section with the simpler related compounds (IX)–(XXVIII) having the P—C_{sp^3} bonds shows that the *trans*-orientation of the P=O and C—Cl bond predominates in all the phosphoryl compounds investigated having the CH_2Cl group (groups) and small substituents at the phosphorus atom. The "cisoid" (60° ≥ φ ≥ 300°) orientation of the P=O and O—Alk bonds which has been established is common to phosphoric acid esters. Thus the steric structures of the compounds investigated having different substituents at the phosphorus atom correspond fully to the structures of related derivatives with a single irregular group and do not exhibit any new intramolecular effects.

Consequently, the features discovered previously for molecules with identical groups account fully for the structure of phosphoryl compounds with different substituents.

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The data presented in this review lead to the conclusion that fairly extensive and quite definite information has now been accumulated on the hindered internal rotation about the phosphorus–carbon bond. Modern ideas concerning the nature of various intramolecular effects frequently permit an *a priori* determination of the preferential conformation of a compound which has not yet been studied. However, for subsequent successful conformational investigation of the given class of compounds, containing the P=O group, it is necessary to concentrate attention on the following problems: (1) the determination of quantitative data for the barriers to internal rotations; (2) the improvement and extensive employment of a scheme involving the combined application of the maximum possible number of independent physicochemical characteristics; (3) the estimation of the steric structures of compounds in aqueous media.

Quantitative information about the barriers to internal rotation can be obtained by employing microwave and NMR spectroscopy. However, experimental and theoretical difficulties significantly limit the application of these methods to the class of compounds under discussion. In this case the combination of vibrational spectroscopic and gas-phase electron diffraction methods, which make it possible to draw inferences about the nature of the change in the potential energy in the course of the hindered internal rotation from the torsional frequencies in the spectra and the geometrical parameters of the molecules determined, acquire special importance in this instance.

Analysis of data referring to the group of compounds with different irregular substituents shows that in the case of complex organic compounds the application of any one method cannot lead to a reliable solution of the conformational problem. The increase of the number of physicochemical parameters employed permits the analysis of the compatibility of the characteristics of the conformational equilibria with experimental data. When the number of equations relating the experimental and theoretical physicochemical characteristics corresponds to the number of the possible conformers, one can obtain a rigorous solution of the conformational problem[52]. The employment of the possibilities inherent in the NMR spectroscopic method involving different nuclei is evidently extremely promising for complex systems in this instance.

One should also note that the results presented in this review refer to gaseous, liquid (including solutions in non-polar and polar solvents), or crystalline states of the molecules. In order to assess the problem of the physiological activities of compounds, it is essential to have information about their steric structures in aqueous solutions. Such data are not available for the class of compounds discussed in this review. The present authors have recently obtained the infrared spectra of aqueous solutions of a phosphoryl compound with a halogenomethyl group using an IFS-113 Fourier spectrometer. It was found that in water the ratio of conformers with the *trans*- and *gauche*-orientations of the P=O and C–Hal bonds (0.4:0.6) differs significantly from the ratio in a non-polar medium (CCl_4, 0.9:0.1). The example presented indicates the necessity for a detailed study of the conformational state of compounds in an aqueous medium. At any rate, the neglect of the influence of the aqueous medium on the stereochemistry in the selection of structural elements responsible for the physiological activity of compounds of a given class can lead to erroneous constructions.

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The Macrokinetics of the Thermal Decomposition of Polymers

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The kinetics of the thermal decomposition of thermoplastic polymers have been reviewed. The influence of the external medium—inert and chemically active gases - on the rate of thermal decomposition has been discussed. Heat and mass exchange at the surface of a polymer undergoing degradation, and the influence of the rate of heating and the thermal flux power, have been examined.
The bibliography contains 67 references.

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I. INTRODUCTION

In connection with the continuous increase in the production and use of polymeric materials, their stability to various external factors, including thermal fluxes of different intensities, is acquiring exceptional importance. When a thermal flux acts on a polymer surface, heating and thermal degradation take place, and this is important from a number of viewpoints.

Many polymers are designed for use at high temperatures of the surrounding medium, and may also be subjected to powerful thermal fluxes from flames and other sources. A knowledge of the mechanism of the thermal decomposition of polymers can therefore be used to change their properties to create fire-resistant synthetic polymers.

Thermal degradation processes can be divided into two categories, according to the nature of the heat acting on the polymer (the thermal flux power and the temperature of the surrounding medium). The first corresponds to bulk processes of isothermal degradation of the polymer, and the second to surface degradation of the polymer, usually called linear thermal decomposition.

Detailed discussion of the isothermal degradation of polymers, examination of the theoretical aspects, and attempts to establish the dependence of the mechanism of the decomposition of polymers on their structure have been carried out by a number of workers, and comprehensive monographs on these topics have been written by Jellinek[1], Grassie[2], Madorsky[3], and others[4,5].

The extrapolation of data on isothermal kinetics in a block to the range of rates of degradation usually encountered in surface thermal degradation and combustion is apparently unjustified[6].

To determine the macrokinetic characteristics of combustion, the efficiency of ablation heat protection, the efficiency of fire-resistant polymer coatings, and the parameters of other processes characterised by high temperatures and high thermal fluxes, it is necessary to know the regular kinetic features of the thermal decomposition and the influence of the surrounding atmosphere, the rate of heating of the polymer surface or the thermal flux power, the structure of the polymer, the thermochemical and thermophysical properties of the polymers, etc.

According to existing ideas[5], polymers can be divided into three classes, according to the type of thermal degradation: the first undergo complete degradation with rupture of the main chain; the second type includes the removal of lateral fragments, and these polymers give volatile gaseous products and a coke residue; and the third type consists of cross-linked polymers which give small quantities of volatile products and a large quantity of coke.

Without going into the details of the mechanism of thermal degradation, the main task today is to establish the limiting stage of the thermal decomposition of polymers at high temperatures and the relationship between the macrokinetics of this process and the kinetic characteristics of the low-temperature "isothermal" degradation. This problem can be solved only by analysing published experimental data on high-temperature thermal decomposition.

The simplest case is the thermal degradation and thermal decomposition of thermoplastic polymers, when the polymer is completely converted to gases, without leaving a residue. In this case it is possible to study the phenomenon of high-temperature degradation and thermal decomposition under quasi-stationary conditions. With polymers of the second and third types, however, a carbonised residue will gradually accumulate on the surface of the condensed phase, leading to a continuous change in the conditions of heat and mass transfer at the interface between the gas and condensed phases. The present paper analyses published experimental data on the thermal decomposition of thermoplastic polymers.

II. PROCEDURES FOR STUDYING THE THERMAL DECOMPOSITION OF POLYMERS

A number of methods have now been developed for studying the macrokinetic characteristics of thermal decomposition in the range of temperatures and rates of thermal decomposition not accessible to classical isothermal methods. They are based on the measurement of the rate of mass loss by the specimen being studied, and on the analysis of the volatile products[3]. An important problem is the measurement of the temperature of the surrounding medium, the temperature of the surface of the polymer undergoing thermal decomposition, and the thermal flux at the surface of the specimen.

The composition of the degradation products under the conditions of high-temperature thermal decomposition characterises not only the processes taking place in the condensed phase but also the secondary reactions taking place in the heating zone. Analysis of the dependence of the degradation products of polymers on the temperature of the sur-

rounding medium[7] showed that increase in the temperature of the surrounding medium leads to a significant decrease in the yield of monomer as a result of secondary reactions for polymethyl methacrylate (PMMA), poly-α-methylstyrene, polystyrene (PS), polypropylene (PP), and other polymers (see Table 1). The yield of monomer in the thermal decomposition is strongly influenced by the conditions of the experiment[7].

Table 1. Yield of monomer (mass % of the total quantity of volatile products) in the thermal decomposition of various organic polymers in a vacuum at elevated temperatures[7].

Polymer	T, °C		
	500	800	1200
Polyethylene	0.03	5.5	26.4
Polypropylene	0.4	17.9	15.8
Polyisobutene	36.5	69.0	13.0
Polystyrene	51.0	10.5	0.6
Polymethyl methacrylate	94.2	91.8	12.9
Polytetrafluoroethylene	96.6	91.2	78.1
Poly-α-methylstyrene	100	88.5	37.7

In the methods developed for studying thermal decomposition, the polymer is heated in different ways: 1) by the heat flux from a heated plate[8-13]; 2) by the heat flux from a massive heat-conducting block[14-16]; 3) by a radiant thermal flux[17-19]; 4) by convective heating in a stream of hot gas[20-24]; 5) by the thermal flux from a diffusion flame formed close to the surface of the polymer specimen, which is swept by a stream of gaseous oxidising agent[25-33], etc.

The first studies of the thermal decomposition of polymers were carried out by Schultz and Dekker[8]. The essential feature of their method is that the polymer specimen is pressed with a constant force by means of a load against the flat surface of a metal plate heated by an electric current. The junction of a platinum–platinum/rhodium thermocouple with a diameter (d) of 50 μm was welded to the centre of the plate above the specimen being tested. The heated-plate method was subsequently developed by other workers[9,10,12,13].

Other workers[34,35] used a porous plate instead of a continuous plate to heat the specimens. In their opinion, the use of a continuous plate to study the thermal decomposition leads to an increase in the rate of the thermal decomposition as a result of the elution (erosion) of the molten liquid layer of polymer from the gap between the specimen and the heater by the flux of thermal decomposition products. Many of the data which they obtained, however, show a marked scatter even for materials which sublime. It is possible that in the thermal decomposition of thermoplastic polymers, the liquid layer flowed into the pores of the plate before volatilising, so that the porous-plate technique has not found application in thermal decomposition studies.

The use of massive copper or aluminium blocks instead of a plate heater has been proposed[14] to obtain linear thermal decomposition with the highest possible levels of thermal flux and rate of thermal decomposition. A heater and a thermistor are mounted on the lateral surface of the block. The junction of a microthermocouple is stamped into the lower end face. The system used to supply the specimen and record the rate of linear thermal decomposition was the same as in Ref.8. The instruments with a heating block solved extremely simply the problem of measuring the thermal flux q_s. Thus placing two Constantan junctions separated by a distance l in the lower part of the copper block having a cross-section close to the area of the end fact (S) of the specimen undergoing thermal decomposition makes it possible, from the readings of the resulting differential Constantan–copper–Constantan thermocouple ΔT_{bl}, to find

$$q_s = \lambda_m \Delta T_{bl}/l$$

where λ_m is the thermal conductivity of copper.

In contrast to previous methods in other studies[21,22,24] etc., the surface of the polymer specimen was heated by a flow of heated gases.

In Ref.22, the temperature of the heated gases was varied from 500 °C to 950 °C, and the flow rate was varied in the range 30–60 cm s^{-1}. The temperature of the polymer surface and the temperature profile along the axis of the specimen were measured by introducing Chromel/Alumel thermocouples with a wire diameter of 50 μm.

In Ref.21, the surface of the specimen undergoing thermal decomposition was swept with the exhaust gases from a small laboratory rocket motor—the products of the combustion of a C_3H_8–O_2–N_2 mixture —and the rate of the thermal decomposition was measured. The concentration of oxygen in the surrounding atmosphere varied from 12 mole % to 83 mole %. The temperature of the stream at the end of the rocket motor jet was 1100 °C. The density of the thermal flux was ~20 cal cm^{-2} s^{-1}. The rate of thermal decomposition was determined by the change in the length of the specimen undergoing thermal decomposition when it was swept by the combustion products for 9 s.

In Ref.24, a method for studying the high-temperature thermal decomposition of polymers in a stream of heated gases was proposed, which made it possible to record the mass rate of thermal decomposition, the temperature of the polymer surface, and the temperature of the stream of gases.

Polymer specimens with an initial mass of ~$(2-3) \times 10^{-3}$ g and initial diameter d_0 = 1–1.5 mm were taken for the study of the thermal decomposition. The specimen was placed on the junction of a Pt–Pt/Rh thermocouple (wire diameter 20 μm), the ends of which were brought through a two-channel sheath with diameter 1 mm and through an amplifier to the recording apparatus. The thermal decomposition was carried out in a stream of gases, heated by an electric furnace, and the rate of flow was kept constant (4 cm s^{-1}). When introduced into the furnace, the polymer specimen melted, covered the junction of the thermocouple, and hung from it as a liquid drop. The thermocouple junction was then in the surface layer of the specimen, and recorded a temperature close to the temperature of the surface of the polymer. The change in the mass of the specimen was recorded using an electronic microbalance based on an MKh-1S mechano-electronic device—an electronic valve with a moveable anode. The signal from the mechano-electronic device was passed through an electronic transformer and amplifier and recorded by an N-115 oscillograph. Typical curves giving the change in the mass of the specimen and temperature are shown in Fig.1. When the specimen is introduced into the stream of heated gases, in the first period (I) the specimen is heated to a temperature T_s, which changes little during the thermal decomposition of the polymer specimen. When the thermal decomposition is complete, the thermocouple records the temperature of the stream T_∞.

The degradation of small polymer specimens in a stream of heated gases under the conditions of thermal decomposition and combustion has been studied[26]. The experimental assembly included two electrical heating coils, between which the polymer specimens (diameter 1–2 mm) were placed, at the

end of a horizontal glass fibre. The coils were heated to ~1000 °C. The diameter of the specimen was measured photographically during the thermal decomposition and combustion to within 1.27×10^{-3} cm. The temperature of the polymer surface was estimated using a thermocouple, on which the polymer specimen was placed. As in the previous case, the temperature of the specimen increased rapidly in the first period, after which it remained practically constant until the specimen disappeared completely, when it increased sharply, recording the temperature of the external medium. The moment of complete volatilisation of the polymer was recorded photographically.

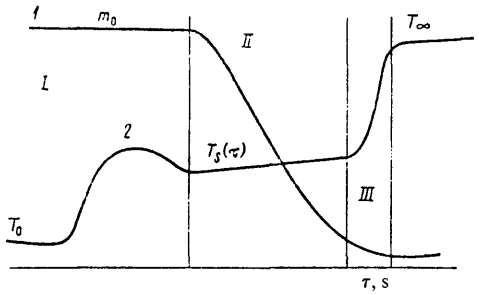


Figure 1. Change in mass (m) (*1*) and temperature (*2*) during thermal decomposition: *I*) heating of the polymer, *II*) thermal decomposition, *III*) recording of the flow temperature T_∞.

To increase the thermal flux at the polymer surface under conditions in which the polymer was swept by a stream of heated gases, a method was developed[25] in which a planar diffusion flame was established above the surface of the polymer. The temperature profile in the condensed phase was measured by a thermocouple placed inside the specimen. Cylindrical PMMA specimens with diameter 1.9 cm and length 3.71 cm were studied. The rate of linear thermal decomposition was determined in the stationary region by measuring the time required for the thermal decomposition of a specimen with a thickness of 1.27 cm. In addition to the thermocouple method, the temperature of the surface was measured using spectral methods, by recording the emission spectra of PMMA at a wavelength of 5.8 μm (the characteristic band of the C=O bond in the monomer), and determining T_S from their intensity. The optical measurements of the temperature of the surface (T_{SO}) gave a reproducible dependence of the temperature on the concentration of oxygen in the stream. The values of T_{SO} obtained were only a few degrees higher than the values measured by other methods.

The thermocouple measurements were carried out using Pt–Pt/Rh thermocouples with diameter 15 μm. In all cases, a region of relatively slow increase in temperature was observed before the thermocouple came out on to the surface. The extent of this region decreased sharply with increase in the rate of thermal decomposition. From the change in the nature of the thermocouple noise, it was concluded that there is a liquid layer on the surface of the PMMA undergoing thermal decomposition. The temperature profile in the condensed phase under the conditions of "quasi-stationary" thermal decomposition was assumed to obey Mikhel'son's equation[36]

$$T_{(x)} - T_0 = (T_s - T_0)\exp(-Ux/a) \quad (1)$$

where x is the distance from the surface, $T_{(x)}$ the current temperature, T_0 the initial temperature, T_S the temperature of the surface, a the coefficient of temperature change in the polymer, and U the rate of linear thermal decomposition. The authors[25] found the temperature of the surface by analysing their temperature profile data using the semilogarithmic relationship of Eqn.(1).

Other authors[34,37] studied combustion processes using an apparatus similar to that developed in Ref.25. An optical device was used to keep the surface of the specimen at the same distance from the front of the jet through which the oxidising agent was passed. In Ref.38 the polymer specimen was swept not by a counter stream but by a stream in the same direction, and "candle combustion" took place. All the measurements of the mass rate of thermal decomposition under the conditions of candle combustion were carried out when stationary conditions had been reached.

In Ref.19, thermal decomposition under combustion conditions was studied using planar polymer discs with thickness 3–5 cm and thermal decomposition surface area from 60 cm^2 to 100 cm^2. The specimen was placed in a quartz tube of length 61 cm and diameter 17 cm. A nitrogen–oxygen mixture with a given O_2/N_2 ratio was passed through the tube at a rate of 50–70 litre min^{-1}. The apparatus was fitted with two additional powerful sources of thermal radiation, which were directed on to the surface of the polymer being studied. The mass rate of thermal decomposition was measured continuously by an electronic balance. To investigate the influence of various factors on the rate of thermal decomposition ($\dot{m}$), the influence of the thermal decomposition surface area on the value of $\dot{m}$ was first studied. Extrapolation of the data on the dependence of $\dot{m}$ on S gave different values of the surface area at which $\dot{m}$ no longer depends on S; 3.0 m^2 for polystyrene, 2.5 m^2 for polymethyl methacrylate, 0.5 m^2 for polyethylene, and 0.3 m^2 for polypropylene.

To exclude completely the influence of heat losses from the specimen to the surrounding medium, that is to eliminate the influence of the surface area of the heated specimen on the mass rate of thermal decomposition, a method was proposed[33] for studying thermal decomposition under the conditions of the diffusion combustion of a spherical specimen completely surrounded by a flame. The polymer specimen with diameter 10 mm was fixed by a quartz capillary-holder on a vertical ceramic tube with outer diameter 1–1.5 mm. This ceramic tube was firmly connected to the horizontal rod of a mechano-electronic device, which recorded the change in the mass of the specimen undergoing thermal decomposition under combustion conditions. The power of the thermal flux to the surface of the polymer was controlled by changing from 20% to 100% the proportion of oxygen in the $N_2 + O_2$ mixture, supplied through a quartz tube with diameter 70 mm. The specimen was ignited by a gas burner, which was switched off immediately after the specimen began to burn. The thermal flux to the polymer surface was measured using a thermocouple probe, the shape of which coincided with the shape of the isothermal surface of the specimen. The temperature profile in the specimen and the temperature of the thermal decomposition surface were measured by a thermocouple placed inside the specimen at a distance of 1 mm from the surface. The diameter of the Pt–Pt/Rh wire used for the thermocouples was 0.02–0.03 mm. The external thermocouple probe was firmly connected to the linear displacement meter, whose readings were recorded on an oscillograph film. The moment when the outer thermocouple probe touched the polymer surface was recorded from the

response of the mechano-electronic device on the oscillograph film, and also visually using a KM-6 cathetometer and time recorder. An advantage of this method is that the change in the mass of the specimen undergoing thermal decomposition and the temperature profile in the gas and condensed phases are recorded on the same time coordinates.

The values of the maximum temperature of the flame (T_f), the temperature of the surface (T_S), and the temperature gradient (dT/dr), determined using the external thermocouple probe, are given in Table 2.

Table 2. Temperature measurements during the combustion of spherical PMMA specimens in an $N_2 + O_2$ atmosphere[33].

O_2, %	T_f, °C	T_S, °C	dT/dr, K cm^{-1}*
20	1350	460	5050
25	1520	480	6200
30	1660	500	7400

*Radius of the specimen in the measurements 4.5 cm.

The temperature of the surface and the temperature gradient at high oxygen concentrations (greater than 30 mass %) were measured by means of an internal thermocouple which emerged into the gas phase; this moment was recorded optically and determined from the sharp break on the curve giving the change in temperature. In Ref.30, an apparatus was proposed for determining the rate of degradation under conditions of thermal decomposition and combustion, in which a cylindrical reaction vessel with diameter 0.8 cm and height 1 cm was connected to a quartz rod, acting as the rod of an electronic balance. In this apparatus it was possible to carry out the thermal decomposition in a stream of air and inert gas. The planar heater, with diameter 0.9 cm, was placed at a distance of 0.8 cm from the specimen surface. The instrument developed makes it possible to record simultaneously the temperature of the specimen undergoing thermal decomposition and the change in its mass.

III. MEASUREMENT OF THE TEMPERATURE OF THE SURFACE OF POLYMERS DURING THERMAL DECOMPOSITION

Data on the kinetics of the degradation of polymers are usually correlated using the Arrhenius expression for the rate of thermal decomposition

$$\dot{m} = A \exp(-E/RT_s) . \qquad (2)$$

If the kinetic data are described by this relationship, the data obtained in one temperature range can be used to predict the behaviour of the polymer in other temperature ranges.

Success in correlation has been restricted to the knowledge of such quantities as T_S and the thermodynamic properties of a specific polymer[6]. When the experiments are carried out in the low-temperature range up to 300 °C, and when the degradation takes place in the "kinetic range", that is when the characteristic heating time of the specimen is much less than the chemical reaction time, the temperature of the polymer is equal to the temperature of the reaction vessel or the temperature of the surrounding medium.

Shteinberg[15] examined the physical picture of the endothermic bulk decomposition (gasification) of a sphere of substance whose kinetics corresponded to Eqn.(2). By introducing characteristic time scales, namely the heating time of the sphere

$$\tau_h = \frac{r^2}{a}$$

where r is the characteristic dimension of the specimen, and a is the thermal conductivity, and the decomposition time of the substance at a temperature T_S

$$\tau_r = [K_0 \exp(-E/RT_s)]^{-1}$$

he estimated the relative thickness of the reaction layer Δ.

At comparatively low temperatures T_S (Fig.2*a*), $\tau_h \ll \tau_r$, and all the substance can be heated to a temperature $T \cong T_S$ (the temperature gradient along the thickness of the specimen is practically zero) long before any significant fraction of it decomposes, $\Delta = r$. With increase in T_S (Fig.2*b*), the decomposition time τ_r becomes commensurate with the heating time τ_h, and $\Delta < r$. In the limit when $\tau_h/\tau_r \gg 1$ (Fig.2*c*), the thickness of the reaction layer is much less than the thickness of the material $\Delta/r \ll 1$, that is degradation takes place close to the hot surface, and moves together with the heating wave. The temperature profile in the condensed phase is determined by the ratio between the rate of movement of the heating wave and the thermophysical characteristics of the polymer specimen in accordance with the Mikhel'son equation[36]. When the degradation is carried out under thermal decomposition conditions, the temperature measurement involves considerable difficulties. In early studies of linear thermal decomposition by the heated-phase method[8–13], and also in thermal decomposition by a heated metal block[14–16], the thermocouple designed to record the surface temperature was fixed in the metallic heater. The temperature of the heater was taken as the temperature of the surface.

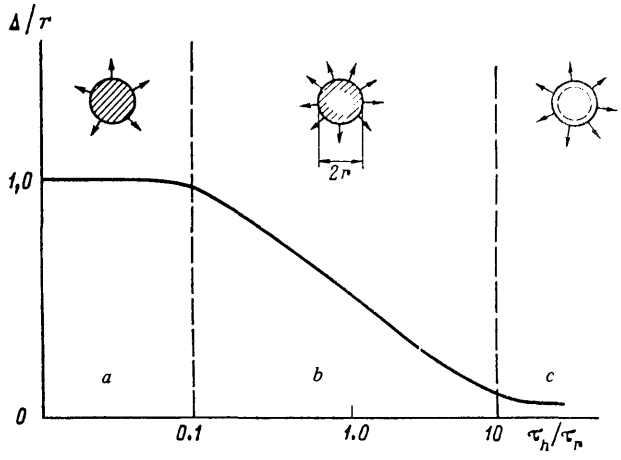


Figure 2. Dependence of the relative thickness of the reaction layer on the ratio of the characteristic times of thermal relaxation τ_h and decomposition τ_r.[15]

Cantrell[10] was the first to draw attention to the fact that the temperature of the surface undergoing thermal decomposition was different from the temperature of the heated block.

With change in the temperature of the heater T_0 from 8 °C to 60 °C, the rate of the linear thermal decomposition of solid carbon dioxide increased by a factor of less than 2, and the temperature of the surface T_S increased from −52 °C to −42 °C. An interesting feature is the appreciable superheating of the surface of dry ice compared with the temperature of equilibrium sublimation, corresponding to a pressure of gas in the film of ~1 atm. It was pointed out that for small T_0, $T_S \cong T_0$, and at high T_0 and high rates of linear thermal decomposition, the effect of the film may be significant, and $T_S < T_0$. Cantrell examined the problem of the transfer of heat in the gas gap formed by the linear thermal decomposition between the heater plate and the polymer, and obtained an equation relating the thickness of the gap (z) to the geometric dimensions of the specimen (r), the rate of linear thermal decomposition (U), the density of the substance (ρ), the viscosity of the thermal decomposition products (γ), and the force (W) pressing the polymer against the heated surface

$$z = \frac{3}{2}(\pi r^4 \gamma \rho U / W)^{1/3} . \quad (3)$$

In his experiments on the linear thermal decomposition of PMMA, Shteinberg[16] recorded the linear rate of decomposition and the thermal flux to the specimen surface q_1, which is given by:

$$q_1 = \lambda (T_0 - T_s)/z \quad (4)$$

where T_0 is the temperature of the heater. Eqns.(2)–(4) were used to calculate the values of ΔT, which are given in Fig.3.

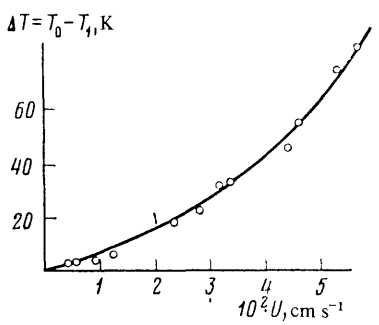


Figure 3. Change in the temperature drop through the gas film with increase in the rate of thermal decomposition of PMMA.[14]

The values of the thermophysical constants of the gas in the calculations were taken for the heavy hydrocarbon octane at the temperature of the plate. For the highest rates of thermal decomposition achieved in the experiments, the calculated thickness of the gas gap did not exceed 30 μm.

Tkachenko and co-workers[14] studied the thermal decomposition of linear and cross-linked PMMA. The temperatures of the surface of the material undergoing thermal decomposition at medium rates of thermal decomposition were calculated as in the previous case, but for high rates, assuming that T_S is constant, the temperature was found graphically from the equation:

$$\frac{mr}{W^{1/3}} = \left(\frac{32}{\pi}\right)^{1/3} \frac{\lambda (T_0 - T_s)}{\nu^{1/3} [c (T_s - T_\infty) + Q]} .$$

The values of T_S obtained were 450 °C for linear PMMA, and 475 °C for cross-linked PMMA.

In a study of the linear thermal decomposition of PE and PMMA,[23] the dependence of the temperature of the surface of the polymers undergoing thermal decomposition on the temperature of the surrounding medium was measured, and it was shown that they gradually increase.

A study of linear thermal decomposition in a stream of heated gases in the temperature range 500–950 °C [22,39] showed that the temperature of the surface and the temperature profile in the condensed phase are the same, irrespective of the conditions of the experiment.

Table 3. Temperatures of the surface (T_S) in the combustion of various polymers[25,40].

Polymer	λ, μm	T_s, °C	
		in air	in oxygen
Polyethylene	6.9	511	570
Polyisobutene	6.9	428	469
Polyester-polyurethane rubber	8.75	—	507
Polypropylene glycol-polyurethane rubber	8.75	—	492
Polymethylmethacrylate	8.75	417.417	477—490.527

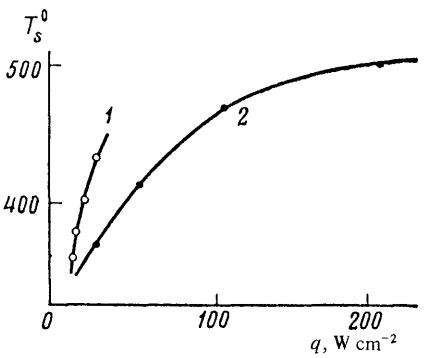


Figure 4. Influence of the thermal flux on the temperature of a PMMA surface during thermal decomposition: *1*) data from Ref.17, *2*) data from Ref.18.

The increase in the rate of linear thermal decomposition was attributed to the increase in the rate of volatilisation of the degradation products from the surface.

Infrared radiation has been used[40] to measure the temperature of the surface of burning fuels and polymer binding agents. This method was used to measure the temperatures of the surface of polymers during combustion in air and in an oxygen atmosphere.

The data in Table 3 show that for combustion in oxygen, T_S is 40–60 K greater than for combustion in air. The same method has been used[25] to determine the temperature of the surface in the thermal decomposition of PMMA during combustion.

Published data[17,18] on the influence of the thermal flux on the temperature of thermal decomposition show that with increase in the thermal flux to a surface, its temperature

increases (Fig.4). The dependence is more marked at low thermal fluxes. The lack of agreement in the published data[17,18] is due either to the inaccuracy of the determination of the thermal flux to the polymer surface or to the inaccuracy of the temperature determination.

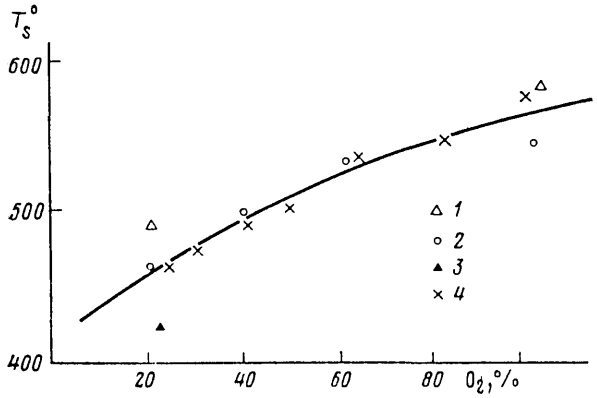


Figure 5. Dependence of the surface temperature of a PMMA specimen undergoing thermal decomposition under combustion conditions on $[O_2]$: *1*) Ref.25, *2*) Ref.26, *3*) Ref.33, *4*) Ref.44.

Table 4. Surface temperatures and combustion constants for polymers in air[26].

Material	T_s, °C	K, s cm^{-2}	
		expt.	theor.
Polyethylene	538.500*	39.8	57
Polypropylene	528	40.4	—
Nylon-6	542	29.4	—
Polymethylmethacrylate	416	36.3	57
Polystyrene-butadiene	—	44.1	—
Polyvinyl acetate	—	25.4	—
Cellulose acetate	309	6.1	—
Polystyrene	480** 494 480*	57.6	61
Polycarbonate	578	11.6	—
Phenol resin	—	80.5	—
Polyamide	—	29.7	—

* —[43], ** [42].

The influence of the oxygen concentration on T for the surface of a burning PMMA specimen was studied by other workers[34,41], and the results are given in Fig.5.

The experimental values of the temperatures of the surface and the rates of combustion for a number of polymers are given in Table 4.

Systematic studies of the influence of the temperature of the surrounding medium on the temperature of the surface of thermoplastic polymers undergoing thermal decomposition in a stream of heated gases have been carried out[24], and the results are given in Table 5.

IV. INFLUENCE OF OXIDISING AGENTS AND CHEMICALLY ACTIVE GASES ON THE THERMAL DECOMPOSITION OF THERMOPLASTIC POLYMERS

Studies carried out by many authors on the influence of oxygen on the rate of "bulk" degradation, studied thermogravimetrically, have shown that the presence of oxygen in the surrounding atmosphere usually leads to a marked increase in the rate of the bulk degradation of thermoplastic polymers[44,45]. In thermal decomposition, however, we are dealing with much higher temperatures, thermal fluxes, rates of heating of the specimen, and rates of degradation, so that it was necessary to determine the role of chemically active gases and oxygen in this range.

Table 5. Values of T_s (°C) in the thermal decomposition of thermoplastic polymers in a stream of heated gases[24].

Polymer	T_s					
	500	600	700	800	900	1000
PMMA	410	440	460	470	480	485
POM	450	490	515	530	535	540
PS	465	500	525	545	555	565
PE	485	535	570	595	610	620
PP	480	525	560	585	600	610

In Ref.21, the surface of a porous polymer was heated in the exhaust from a laboratory jet motor—the combustion products of a C_3H_8–O_2–N_2 mixture. The concentration of oxygen in the surrounding atmosphere was varied from 12 mole % to 83 mole %. A study of the rates of the thermal decomposition of PS and PMMA showed that the rate of the thermal decomposition is not sensitive to oxygen. In another series of experiments, a porous specimen was used and the concentration of any test gas passed through it was accurately controlled. The influence of N_2, O_2, ClO_3F, NO, NO_2, Cl_2, HCl, NH_3, and SO_2 on the thermal decomposition of PS and PMMA was studied. The rate of the thermal decomposition of PMMA and PS decreased with increase in the rate of supply of the test gases, but the introduction of NO_2 and Cl_2 led to a slight increase in the rate of the thermal decomposition of PS. The decrease in the rate of degradation with increase in the supply of test gases was related to the increase in the proportion of heat used up in heating the gas, and the decrease in the heat used to heat the polymer.

The influence of the concentration of oxygen on the thermal decomposition of PS and PMMA in a stream of gas heated to a temperature of 700 °C has been studied[22]. Increase in the O_2 concentration has no influence on the rate of the linear thermal decomposition of PS, and leads to a slight increase in the rate for PMMA.

A study of the influence of oxygen on the rate of the linear thermal decomposition of polystyrene, styrene–butadiene copolymers, and mixtures of polystyrene with o-phthalic acid, maleic acid, and propylene glycol[46] showed that at rates of thermal decomposition comparable with the rates observed in the combustion of polymers, oxygen has no influence on the rate of the linear thermal decomposition.

In Ref.24, the influence of the composition of the surrounding atmosphere was investigated by studying the thermal decomposition of PMMA in a stream of helium, nitrogen, and air. The values of the "volatilisation" constants for spherical specimens in a stream of heated gases, and their thermal conductivities, are given in Table 6.

At medium temperatures of the surrounding medium, the volatilisation constant is greater in helium, in which the thermal conductivity is almost ten times that for nitrogen and air. With increase in T_∞, this difference decreases, as a result of the increase in the contribution of radiation from the heating furnace to the total thermal flux. Thus at a temperature of ~1000 °C, the radiative thermal flux to the polymer surface is ~0.1 cal cm^{-2} s^{-1}, and the convective thermal flux ~0.05 cal cm^{-1} s^{-1}.

Table 6. Volatilisation constants 10^3 K, cm^2 s^{-1} for PMMA.

Gas streat	10^6 λ, cal $cm^{-1}s^{-1}K^{-1}$*	T_∞°					
		400	500	600	700	800	900
Nitrogen	98	0.5	2.5	4.8	7.0	9.6	13.0
Air	99	0.4	2.2	4.2	6.2	—	—
Helium	670	1.5	3.0	5.0	7.5	11.0	15.5

*The values of λ were taken for the gases at a temperature of 500 °C.[47]

From the neutron activation analysis of hot molten polypropylene[38], it was concluded that oxygen from the surrounding atmosphere is sorbed in the molten polymer layer. Examination of the thermal balance showed that an appreciable proportion of the heat is liberated in oxidation at the surface. It was concluded that if the contribution from external parameters is excluded, the combustion of the polymer is determined by its stability towards thermal oxidation.

On the basis of the results of Ref.29, the authors of Ref.48 examined the propagation of a flame over a polypropylene surface. They found that the temperature of the polymer surface increases from 350 °C to 500 °C with increase in the concentration of oxygen in the stream from 21% to 28%. As in the previous study, they found that the temperature of the flame remains constant at 1308 °C. This was taken as proof of the participation of oxygen in the thermal decomposition of polypropylene and the heating of the surface. Although analogous data were obtained for PMMA, it was stated that in the case of PMMA, surface oxidation does not take place.

The ^{13}C NMR spectra of molten PMMA formed during the combustion of a specimen coincide with the spectra of the original specimen[49]. This confirms indirectly that oxygen does not take part in the reaction in the condensed phase. The combustion of PMMA and MMA in a stream of oxidising agent has been studied, and the temperature profiles and the profiles of the products of the thermal decomposition of the polymer and their subsequent transformation obtained[50]. From an analysis of the profiles of the concentrations of the products in the gas phase and the temperature profiles, it was concluded that the earlier suggestion[29,37,48] that oxidation processes take place on the surface of the condensed phase is not justified. Other conditions being equal, the escape of oxygen through the diffusion flame is the same for the polymer and the monomer, and amounts to 0.5 mole %. This quantity of oxygen is too small for an exothermic reaction to take place on the surface. Oxygen can catalyse only the thermal oxidation of the gaseous thermal decomposition products, but cannot have any significant influence on the thermal decomposition of the condensed phase, since there is a fairly powerful stream of monomer from the surface.

V. MACROKINETICS OF THE THERMAL DECOMPOSITION OF THE POLYMERS

As shown in section I, in the thermal decomposition of polymers, the supply of heat to the surface can take place by one single mechanism or by several mechanisms simultaneously (radiation, convection, conduction, etc.).

Thermal decomposition usually takes place under "quasi-stationary" conditions, when the heat absorbed by the chemical degradation reaction is equal to the heat supplied to the polymer. To determine accurately by formal kinetics the dependence of the mass rate of degradation on the external conditions in each specific case it is necessary to solve the non-stationary thermal conductivity equation, after which the familiar temperature distribution $T(x, \tau)$ within the specimen can be used to determine the mass rate of degradation as

$$\frac{dm(x,\tau)}{d\tau} = K_0 \int_V \rho \exp\left[-\frac{E}{RT(x,\tau)}\right] dV$$

where ρ is the density of the material, K_0 the pre-exponential factor, and E the activation energy of degradation.

The analytical solution of the non-stationary thermal conductivity equation with a sufficient accuracy, even in the spherically symmetrical case for the bulk thermal degradation in a molten polymer and varying thermal flux over the surface of a sphere represents an extremely complex problem, and can be carried out only in particular cases. For many thermal decomposition problems, however, it is sometimes sufficient to examine only the thermal balance equation:

$$q_1 + q_2 + q_3 = \frac{dm}{d\tau} \cdot L + q_4$$

where q_1 is the radiation thermal flux, q_2 the convection or conduction thermal flux, q_3 the thermal flux through the specimen holder, $\frac{dm}{d\tau} \cdot L$ the absorption of heat as a result of the chemical degradation reaction (L is the heat of gasification), and q_4 is the heat used to heat the specimen. The thermal flux of the radiation from the surrounding non-isothermal cavity with an emissivity different from unity is determined in accordance with the geometry of the surroundings and the arrangement of the specimen relative to the surroundings, and is proportional to the emissivity of the material ε.

For an isothermal cavity with a surface area much greater than the surface area of the spherical specimen, the surface absorption is given by[51]:

$$q_1 = 4\pi r^2(\tau)\varepsilon\sigma(T_1^4 - T_s^4)$$

where $r(\tau)$ is the current radius of the sphere, and T_1 and T_S the temperatures of the cavity and the polymer surface.

If the thermal decomposition is carried out in a laminar stream of hot gas, the convective thermal flux to the polymer surface is given by[52]

$$q_2 = \frac{\overline{Nu} \cdot \lambda_f}{d(\tau)} (T_2 - T_s) \cdot S$$

where $d(\tau)$ is the diameter of the sphere, S the area of the sphere, T_2 the temperature of the gas, λ_f the thermal conductivity of the gas at a temperature $(T_2 + T_3)/2$, $\overline{Nu}$ the Nusselt number, which is determined by the geometric dimensions of the specimen and the physical conditions of flow, and $\overline{Nu} = f(Re, Pr)$ is a function of the Reynolds and Prandtl numbers.

For a sphere swept by a gas stream $Pr \approx 1$, and for small $Re \to 0$, $\overline{Nu} \to 2$, and for intermediate values $Re = (0-100)$, $\overline{Nu} = 2(1 + 0.08Re^{2/3})$.[53]

For the thermal decomposition of a polymer specimen in a stationary heated atmosphere, the parameter describing the nature of the motion is not *Re* but another dimensionless quantity—the Grashof number[53]

$$Gr = gd^3\gamma\Delta T/\nu^2$$

where g is the acceleration due to gravity, ν the kinematic viscosity, γ the coefficient of volume expansion of the medium, and ΔT the temperature difference responsible for the convection. For gases, $\gamma \sim 1/T$ and

$$Gr = \frac{gd^3}{\nu^2} \cdot \frac{\Delta T}{T} .$$

For heat exchange by conduction, the thermal flux to the surface of a sphere will be given by the equation

$$q_2' = \lambda_f \left.\frac{dT}{dr}\right|_{r=r(\tau)} \cdot S$$

where $S = 4\pi r^2(\tau)$ is the area of the surface of the sphere.

The thermal flux q_3 must be determined or calculated in each specific case, depending on the type of holder (quartz capillary, support, thermocouple wire, etc.). In thermal decomposition experiments it is desirable to decrease the flux q_3, since it is difficult to estimate its magnitude with sufficient accuracy, as it may show a complex dependence on the geometric dimensions. q_3 can be estimated for the thermal decomposition of a specimen on the junction of a Pt–Pt/Rh thermocouple with diameter $\delta = 0.02$–0.05 mm. The emissivity of platinum is assumed to be zero[47,54]. The purely convective heating of the wire is examined under the most favourable conditions, when its axis of symmetry is perpendicular to the thermal flux. The thermal conductivity equation for the temperature distribution along the axis of the wire from the surface of the specimen has the form

$$\lambda_{Pt} \cdot \frac{\partial^2 T(x)}{\partial x^2} = \frac{\overline{Nu}\lambda_f}{2\delta} [T_2(x) - T_3(x)] \frac{dS}{dV} \qquad (5)$$

with boundary conditions

$$T_3(x)|_{x=0} = T_s,\ T_3(\infty) = T_2(\infty)$$

where $T_3(x)$ and $T_2(x)$ are the temperatures of the wire and the gas at a distance x along the axis of the thermocouple, $dS/dV = 2\pi\delta\Delta x/\pi\delta^2\Delta x = 2/\delta$; and λ_{Pt} the thermal conductivity of platinum. For the gas it will be assumed that $Pr = 1$. The temperature fields and the flux rate fields at the polymer surface are then similar

$$\frac{T_2 - T_3}{v_0} = \frac{T_2(x) - T_s}{v(x)} \qquad (6)$$

where v_0 and $v(x)$ are the flux rates at a sufficient distance from the specimen and at a distance x from the specimen.

For small values $1 < Re < 4$, the following equation is applicable[52]

$$Nu \approx 0.891 \cdot \left(\frac{v_0 2\delta}{\nu}\right) \cdot 0.33 \qquad (7)$$

From Eqns.(6), (7), and (5),

$$\lambda_{Pt}\left[\frac{\partial T_3(x)}{\partial x}\right]^2 = \int_0^\infty \frac{2\lambda_f}{\delta^2}\left[\frac{T_2(x) - T_s}{T_2 - T_3}\right]^{0,33} \cdot 0.891\,[T_2(x) - T_3(x)]\left(\frac{v_0 2\delta}{\nu}\right)^{0,33} dT_3(x) .$$

The maximum value of the integral is obtained for $T_2(x) = T_2$

$$\left.\frac{dT_3(x)}{dx}\right|_{x=0} = \sqrt{\frac{\overline{Nu}}{\delta^2} \cdot \frac{\lambda_f}{\lambda_{Pt}}} \cdot (T_2 - T_3)$$

$$q_3 = 2\lambda_{Pt} \cdot S \left.\frac{dT_3}{dx}\right|_{x=0} = 2\lambda_{Pt}\pi\delta \sqrt{Nu\frac{\lambda_f}{\lambda_{Pt}}} (T_2 - T_s) .$$

The maximum value of q_3 for the thermal decomposition of a polymer drop on a Pt–Pt/Rh thermocouple ($d = 0.02$–0.05 mm, $\lambda_f = 0.6 \times 10^{-4}$ cal cm^{-1} s^{-1} K^{-1}, $Nu = 0.5$, $\delta = 0.0025$ cm, $\lambda_{Pt} = 0.8$ cal cm^{-1} s^{-1} K^{-1}, ($T_2 - T_S \cong 250°$) is ~0.5×10^{-2} cal cm^{-2} s^{-1}.

To estimate q_4, the heat used to heat the specimen, it is necessary to solve the non-stationary thermal conductivity equation. For the thermal decomposition of a uniformly heated specimen, however, this term can be neglected. For large values of *Bi*, the surface degradation of a spherical specimen should take place with a quasi-stationary temperature profile, and q_4 will decrease with decrease in the current radius of the sphere, since *Bi* decreases. For high initial radii of a spherical specimen and high values of *Bi*, the temperature profile in the condensed phase will tend to the Mikhel'son distribution.

The heating term tends to the value $q_4 = c\rho U(T_S - T_0)$ or

$$q_4 = \frac{dm}{d\tau} \cdot c \cdot (T_s - T_0)$$

and this term can be combined with $L \cdot \frac{dm}{d\tau}$ to give:

$$q_1 + q_2 + q_3 = \frac{dm}{d}[L + c(T_s - T_0)] = \frac{dm}{d\tau} L_{eff} .$$

Thus depending on the diameter of the sphere, different effective heats of gasification of PMMA are obtained, from ~200 cal g^{-1} [55] for the completely heated specimens (diameter up to 1–2 mm), to ~400 cal g^{-1} [19,26] for linear thermal decomposition (large diameters).

For a heated drop of polymethyl methacrylate, the radiation flux for a drop diameter of about 1 mm and a temperature of the wall of the heater of 1000 °C is ~0.10 cal cm^{-2} s^{-1}. The degree of blackness of the polymer is 0.9.[42,54] The convective flux in this case is ~0.05 cal cm^{-2} s^{-1}. The value of q_3 is always smaller than 0.5×10^{-2} cal cm^{-2} s^{-1}, so that q_3 can be neglected, compared with the thermal flux. The thermal decomposition of the heated drop for a constant temperature throughout its volume is proportional to the mass of the specimen, that is

$$\frac{dm}{d\tau} = mK_0 \exp(-E/RT_s) .$$

The thermal balance equation with allowance for convection and radiation can be written as:

$$\frac{dm}{d\tau} = mK_0 \exp(-E/RT_s) = \frac{1}{L_{eff}} \cdot \sum_i q_i = \frac{S}{L_{eff}}\left[\varepsilon\sigma(T_1^4 - T_s^4) + \frac{Nu\lambda_f}{d}(T_2 - T_s)\right] \qquad (8)$$

where L_{eff} is the heat of gasification of the polymer.

The kinetic curve for the thermal decomposition of PMMA in Fig.1 gives the mass loss and the change in the temperature of the polymer specimen. Fig.1 shows that in the first period before the polymer specimen has melted, the thermocouple records the mean temperature between T_S and T_∞, but when the specimen has been heated and melted, it covers the junction of the thermocouple, which records the temperature of formation of the drop T_S.

In this period there is a considerable change in the density of the polymer sphere from 1.19 g cm^{-3} to ~0.8 g cm^{-3}, after which the density remains practically constant. The decrease in the density is due to the increase in the volume[26] (surface area) as a result of the formation of bubbles of the degraded monomer in the bulk. The monomer formed cannot leave the polymer surface immediately, since the rate of formation of the gas phase is greater than the rate of diffusion of the

bubble to the surface. With increase in the temperature of the specimen, the viscosity decreases, and the size of the bubbles reaching the surface is stabilised, and in this range (region II) it may be assumed that ρ is constant and equal to ~0.8.

Region III is characterised by small dimensions of the polymer drop, and in this region it is not possible to neglect the supply of heat through the holder (in the present case through the thermocouple) in the thermal balance equation.

Region II, in which the main mass loss takes place during thermal decomposition, is characterised by a constant smooth increase in the temperature of the drop from T_{s1} to T_{s2} (here we are dealing with the temperature of the entire drop, and not its surface, since all the specimen "boils" vigorously and there is good heat exchange within it, $dT/dr \to 0$).

To understand the increase in temperature in region II, Eqn.(7) is transformed, with the assumption that ρ = const, to the form:

$$L_{\text{eff}} K_0 \exp(-E/RT_s) = \frac{7{,}5\varepsilon\sigma(T_1^4 - T_s^4)}{d} + \frac{7{,}5\lambda_f Nu(T_2 - T_s)}{d^2} \quad (9)$$

It is obvious that with change in T_S by 30–40 K, the difference $(T_1^4 - T_S^4)$ remains practically unchanged, but the difference $(T_2 - T_S)$ decreases by ~5–7%. Thus by introducing the symbols

$$75\varepsilon\sigma(T_1^4 - T_s^4)/L_{\text{eff}}K_0 = A,\ 75\lambda_f Nu(T_2 - T_s)/L_{\text{eff}}K_0 = B_0$$

Eqn.(9) can be transferred to:

$$\exp(-E/RT_s) = \frac{A}{d} + \frac{B}{d^2} \quad (10)$$

Eqn.(10) shows that with decrease in the diameter during the experiment, both terms in the right-hand side increase, leading to an increase in T_S. To follow the dependence of the temperature of the heated drop T_S on the magnitude of the thermal flux, the diameter of the drop in Eqn.(9) is fixed:

$$d = \text{const};\ \frac{75\varepsilon\sigma}{dL_{\text{eff}}K_0} = C;\ \frac{75\lambda_f Nu}{d^2 L_{\text{eff}}K_0} = D$$

$$\exp(-E/RT_s) = C(T_1^4 - T_s^4) + D(T_2 - T_s). \quad (11)$$

Fig.6 gives the graphical solution of Eqn.(11), the intersection of curves *1* and *4*, and gives the required "quasi-equilibrium" temperature of the polymer specimen during thermal decomposition. It is obvious that with increase in the thermal flux to the polymer at a fixed diameter, the temperature of the specimen increases. For thermal fluxes which are not too large, there is only a slight change in the value of T_S.[56]

A number of papers[18,23,24,29,33] give data on the dependence of T_S for various thermoplastic polymers on either the thermal flux power or the temperature of the stream and the temperature of the radiant source, confirming the above conclusions.

Published data[24] on the mass rates of thermal decomposition and the corresponding temperatures were used to obtain graphically (Fig.7) the values of the kinetic parameters for the thermal decomposition of various polymers, given in Table 7.

Data on the thermal decomposition of small and large spherical polymer specimens under combustion conditions have been published[26,33]. The flame zone in the combustion of spherical particles lies close to the polymer surface, and heat exchange between the flame and the surface of the sphere takes place by conduction[33]. According to the theory developed[57–60] for the combustion of hydrocarbon liquids from porous spheres and the combustion of single droplets, the mass rate of combustion can be represented as

$$\frac{dm}{d\tau} = \frac{4\pi\lambda_f r}{c_p} \ln\left[1 + \frac{c_p(T_f - T_s)}{\Delta H - a}\right] \quad (12)$$

where c_p is the heat capacity, $\Delta H = (L + c_p\Delta T)$ the enthalpy of gasification of the polymer, $a = Ra/\frac{dm}{d\tau}$ defines the contribution of the radiation from the flame, and T_f is the temperature of the flame. Eqn.(12) was obtained assuming conductive heat transfer by integrating the thermal flux from the flame over the surface of the specimen. Since the flame of thermoplastic polymers is transparent, the term *a* can be neglected, so that the integration of (12) with respect to time gives the law governing the change in the dimensions of the specimen during thermal combustion

$$d^2 = d_0^2 - \frac{8\lambda_f}{c_p\rho} \ln\left(1 + \frac{c_p\Delta T}{\Delta H}\right) \cdot \tau$$

Introducing the symbol

$$\frac{8\lambda_f}{c_p\rho} \ln\left(1 + \frac{c_p\Delta T}{\Delta H}\right) = K$$

gives

$$d^2 = d_0^2 - K\tau$$

the law obtained for the volatilisation of a drop of liquid[61].

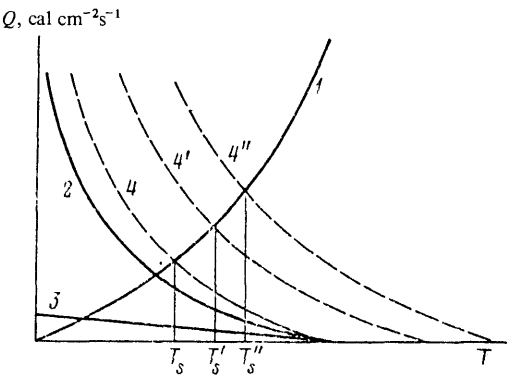


Figure 6. Graphical solution of Eqn.(11).

Table 7. Activation energies of the thermal decomposition of PMMA, PS, and PE.

Polymer	Data from Ref. 24	Other data	Refs.	Polymer	Data from Ref. 24	Other data	Refs.	Polymer	Data from Ref. 24	Other data	Refs.
PMMA	38	30	[3,51]	PE	35	45	[51]	PS	46	63	[51]
		31	[1]			20÷25	[75]			55	[5]
		29.6	[4]			46÷66	[1]			45÷55	[3]
		74	[25]			63	[5]			35	[75]
		40÷43	[15,16]			26÷63	[3]			25÷95	[21]

The change in the diameter of the polymer specimen with time is given in Fig.8.[26]

In this case and in the case of the combustion of large specimens (diameter up to 10 mm),[33] a linear time dependence of the surface area of the sphere is formally observed, since

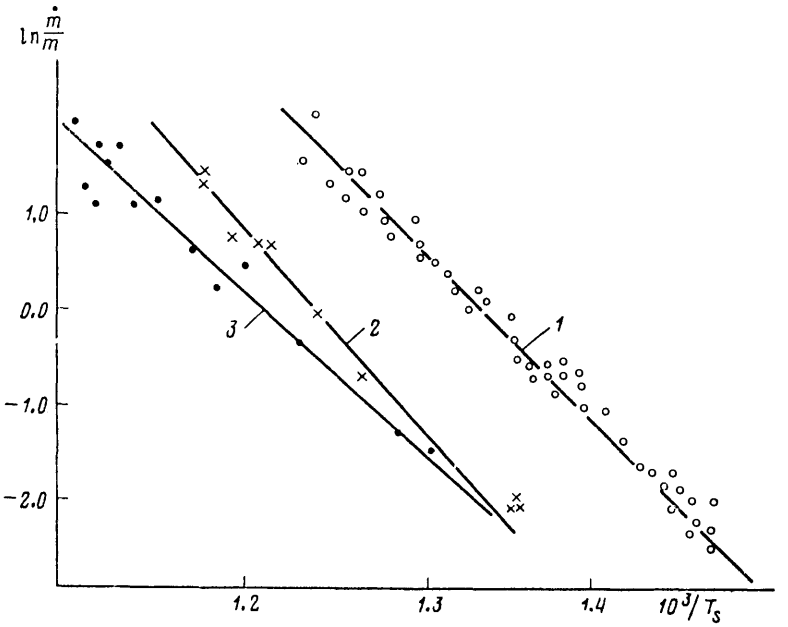


Figure 7. Plot of $\ln \dot{m}/m$ against $10^3/T$ during thermal decomposition: *1*) polymethyl methacrylate, *2*) polystyrene, *3*) polyethylene.

the rate of the process is determined by the rate of heat transfer from the flame to the polymer surface. The exact calculation of the kinetics of the thermal decomposition in the combustion of specimens with a large diameter is an extremely complex problem, because the process is non-stationary. Here, the situation is intermediate between bulk and linear thermal decomposition. In fact, the dependence of $\ln \dot{m}/m$ on $1/T_S$ for a fixed diameter and temperature within the sphere[33] gives a straight line with slope smaller than E but greater than $E/2$.[62] As with bulk thermal decomposition, the absolute values of the mass rates of thermal decomposition are determined by the power of the thermal flux to the polymer surface.

Research workers have paid most attention to the linear thermal decomposition of thermoplastic polymers[8–16]. In this case the temperature distribution in the condensed phase will be determined by Eqn.(2), as confirmed by the data in section II and Ref.43, obtained in a study of heat transfer during the combustion of polymers, and the rate of linear thermal decomposition can be calculated from the relationship[63]

$$U = K_0 \int_0^\infty \exp\left[-E/RT\,(U, x)\right] \mathrm{d}x \,. \qquad (13)$$

The integral was calculated[64] using the Frank-Kamenetskii expansion of the exponent[53] to give

$$U^2 = aK_0 \exp(-E/RT_s) \frac{RT_s^2/E}{T_s - T_0 - \frac{1}{2}\frac{Q}{c\rho}} \,. \qquad (14)$$

The equation obtained is applicable for the model of the linear thermal decomposition of a semi-infinite mass. The effective energy of activation is equal to half the true activation energy. Linear thermal decomposition is usually studied using round rods of finite dimensions, for which heat losses from the lateral surface of the specimen may be significant[65]. Shteinberg[66] examined the regular features of linear thermal decomposition with heat losses, and determined the criterion for the change to the region in which external heat losses can be neglected. By assuming that the temperature field was one-dimensional, that is that the length of the specimen l was much greater than its diameter $d = 2r$, and that the heat losses are limited by external heat exchange between the lateral surface of the specimen and the surrounding medium, the thermal conductivity equation can be written in the form:

$$\frac{\mathrm{d}^2T}{\mathrm{d}x^2} + \frac{M}{\delta}\frac{\mathrm{d}T}{\mathrm{d}x} - \frac{QK_0}{ac}\exp(-E/RT_s) - \frac{Bi}{\delta^2}-(T\ T_\infty)$$

with boundary conditions

$$T|_{x=0} = T_s$$
$$T|_{x\to\infty} = T_\infty$$

where δ is the half-thickness of the plate (or radius of the cylinder), $M = U\delta/a$ is the Mikhel'son (Peclet) number, $Bi = \alpha\delta/\lambda$ the Biot number, and Q the heat of the reaction.

The expression obtained by Shteinberg for the rate of linear thermal decomposition has the form

$$U^2 = \frac{2aK_0T_s^2 \exp(-E/RT_s)}{E\left[(T_s - T_\infty)\left(1 + \sqrt{1 + 4Bi/M^2}\right) - \frac{Q}{C}\right]} \,.$$

For high rates of linear thermal decomposition and relatively small external heat losses, that is for $4Bi/M^2 \ll 1$, the limiting case of the thermal decomposition of a semi-infinite continuum of Eqn.(14) is obtained, and $U \sim \exp(E/2RT_S)$. For low rates, that is $4Bi/M^2 \gg 1$

$$U = \frac{K_0\delta RT_s^2 \exp(-E/RT_s)}{E(T_s - T_\infty)\sqrt{Bi}} \,. \qquad (15)$$

Eqn.(14) shows that with increase in the relative heat losses there is a qualitative change in the nature of the dependence of the rate of linear thermal decomposition on the temperature of the surface, $U \sim \exp(-E/RT_S)$. This is related to the fundamental difference in the dependence of

the width of the reaction zone on the parameters of the process. In the first case, $\Delta \cong a/U$, that is Δ increases without restriction with decrease in the rate of the process. In the second case, $\Delta = \delta\sqrt{Bi}$, that is it is practically constant, since it depends only on the defining dimension of the specimen and the heat exchange criterion Bi. Fig.9 gives the dependence of the rate of the linear thermal decomposition of polymethyl methacrylate on the reciprocal of the temperature of the surface on semilogarithmic coordinates.

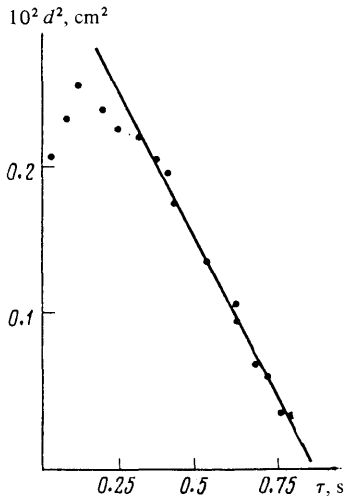


Figure 8. Change in the square of the drop diameter with time.

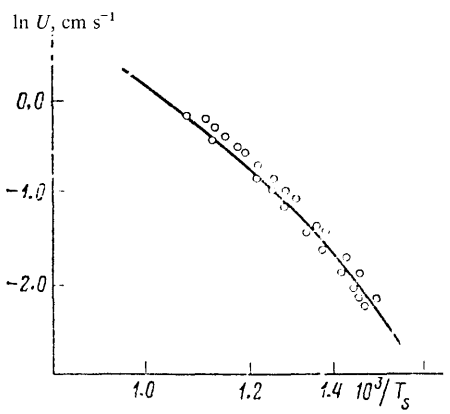


Figure 9. Dependence of the rate of the thermal decomposition of PMMA on $1/T_S$.[16]

Fig.9 shows that in the high-temperature range for large thermal fluxes, the effective value of the activation energy is $E/2$, and the pre-exponential term is equal to K_0. With decrease in the rate of linear thermal decomposition, there is a clearly defined change to the second range, where $U \sim \exp(-E/RT_S)$, that is the activation energy and the pre-exponential term acquire their true values.

It should be noted that the temperature distribution in the condensed phase during thermal decomposition will be more complex than the relationship given by Eqn.(2). Thus the distribution (2) was obtained from the solution of the thermal conductivity equation without a source or sink, with a boundary moving at a rate U. The true temperature distribution in the condensed phase can be obtained only with allowance for the chemical degradation reaction taking place in the surface layer of the condensed phase. In the surface layer of the molten polymer, where intensive degradation is taking place, the bubbles of gaseous degradation products lead to intensive mixing of the melt ("boiling"), and the heat transfer process differs considerably from conduction. The temperature gradient in this layer is $dT/dx \to 0$. For the second zone, where it is possible to neglect the chemical reaction, the temperature distribution along the x axis should be obtained from the solution of the thermal conductivity equation without a source, as in Ref.36, but only with allowance for the temperature dependence of the thermal conductivity coefficient, which increases markedly with increase in T in the range of temperatures produced during linear thermal decomposition on the surface of a polymer.

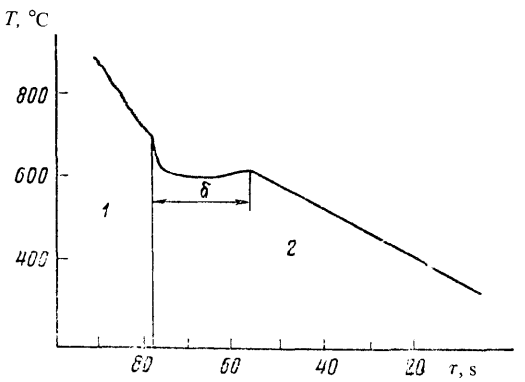


Figure 10. Temperature profile in the condensed phase in the thermal decomposition of thermoplastic polymers[67]; δ is the "boiling layer"; *1*) gas phase; *2*) condensed phase.

The existence of a boiling layer on a polymer surface during linear thermal decomposition was observed by a number of workers[25,67]. Fig.10 gives the temperature profile in the condensed phase obtained in Ref.67 for the thermal decomposition of PMMA. The thickness of the heated layer and the layer of melt in the thermal decomposition of polystyrene is inversely proportional to the rate of the thermal decomposition[43]. The same conclusion was reached in an analysis[25] of data on the thermal decomposition of polymethyl methacrylate Since the temperature distribution, as a result of intensive, heat exchange in the layer δ, is analogous to that shown in Fig.10, the rate of the linear thermal decomposition, in accordance with Eqn.(13), can be written as

$$U = K_0 \int_0^\infty e^{-E/RT(x)}\,dx = K_0 \int_0^\delta e^{-E/RT(x)}\,dx + K_0 \int_\delta^\infty e^{-E/RT(x)}\,dx . \quad (16)$$

Under the conditions of extensive heat exchange in the "boiling" layer, $T(x) \cong$ const in the range $0 \leq x \leq \delta$. Assuming that the reaction takes place at an appreciable rate only in the layer δ, the second integral in Eqn.(16) can be neglected,

and the rate of linear thermal decomposition is

$$U = K_0 e^{-E/RT_s} \int_0^{\delta} dx = K_0 \delta e^{-E/RT_s}$$

and the condition $\delta \sim 1/U$ gives $U^2 \cong K_0 e^{-E/RT_s}$, that is the same dependence of the rate of linear thermal decomposition on the reciprocal of the temperature as in Eqn.(14).

The kinetic characteristics of the degradation of PMMA, K_0 and E, obtained by the study of high-temperature thermal decomposition coincide with the values of K_0 and E obtained for "bulk isothermal" degradation[1,3]. This agreement indicates that on going from the low-temperature to the high-temperature range, the mechanism of the degradation apparently remains unchanged. The conclusions reached by various authors that the mechanism changes may be due chiefly either to the inaccuracy of the measurement of the temperature of the polymer surface during thermal decomposition or to the neglect of the complex macrokinetics in each specific case (the complex temperature profile, which changes with time and with change in the external conditions). Thus to reach final conclusions about the mechanism, it is necessary to carry out new studies with accurate allowance for all factors.

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Enzymic Conversion of Racemates into Aminoacid Enantiomers

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The present state of the art and prospects for further development in the employment of enzymes for the resolution of aminoacid racemates or the conversion of racemates of a series of chemical compounds into optically pure aminoacids are considered. A comparative survey of studies involving the use of aminoacylases, proteases, hydantoinases, α-aminocaprolactam hydrolase, and a number of other enzymes for the preparation of L- and D- aminoacids has been carried out. Examples are presented of processes involving the enzymic resolution of racemates on an industrial scale. The kinetic and thermodynamic features of the enzymic reactions employed have been analysed in detail and the limits in the employment of a particular enzyme for the conversion of racemates into optically pure aminoacids are accounted for.
The bibliography includes 288 references.

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I. INTRODUCTION

The synthesis of optically pure aminoacids has become an increasingly urgent problem of modern biotechnology in recent years. Its solution by purely chemical means involves many difficulties. The chemical synthesis of optically active aminoacids has been achieved so far only in the manufacture of L-3,4-dihydroxyphenylalanine (L-DOPA) by the enantioselective hydrogenation of an α,β-unsaturated derivative in the presence of rhodium complexes of chiral phosphines[1]. The manufacture of L-DOPA is a rare example of a process in which the cost of an extremely expensive catalyst can be neglected in the synthesis of an expensive final product. The industrial chemical synthesis of the remaining aminoacid enantiomers remains at the present time no more than a theoretical possibility.

The manufacture of L- and D-aminoacids by the physicochemical resolution of racemic mixtures of aminoacids obtained by large-scale chemical synthesis (for the chemical synthesis of aminoacids, see the review of Safonova and Belikov[2]) is also not free from disadvantages. Thus the preparation of an enantiomer by the selective crystallisation of a supersaturated solution of the racemate has been achieved only for glutamic acid[3]. The highly effective enantioselective chromatography, which is being activity developed at the present time, has so far found practical applications only in the preparation of optically active compounds labelled by radioactive isotopes[4]. The available methods for the selective crystallisation of the diastereoisomers of aminoacids and any other optically active compounds require the search for and synthesis of the latter, which limits the practical application of this method.

New possibilities for the synthesis of aminoacids have arisen in connection with the development of genetic engineering methods which have given rise to the highly effective industrial production, in the first place of L-lysine, L-histidine, L-arginine, L-threonine, L-isoleucine, and L-valine[5]. The difficulties involved in the employment of this technology are associated primarily with the isolation of the required compond from the culture liquid containing other metabolic products, including many physiologically active compounds, and also with the establishment and maintenance of the properties of the producing agent.

One of the promising ways of obtaining optically pure aminoacids involves the use of individual enzymes. There are two fundamental possibilities for the enzymic preparation of aminoacid enantiomers. The first involves the synthesis, catalysed by many enzymes (aspartate ammonia-lyase, L-tyrosine phenol-lyase, L-tryptophan indole-lyase, phenylalanine ammonia-lyase, etc.), of L-aminoacids from optically inactive precursors, for example, of L-tryptophan and L-tyrosine from ammonia, pyruvate, indole, or phenol[6]. In the present review we shall not discuss the possibility of the employment of this approach to the synthesis of aminoacids, since it has already been considered in detail[7,8].

The second possibility of employing individual enzymes consists in the enzymic conversion of the simplest racemic aminoacid derivatives into the optically pure L- and D-aminoacids. Such enantioselective enzymic reaction results in the formation of a single unreacted optical isomer and the other optical isomer which has undergone chemical modification. The resulting differences between chemical properties make it possible to separate them readily. The presence of two fairly reactive groups in the aminoacid molecule (the carboxy- and amino-groups), linked to the asymmetric carbon atom, permits a large number of similar enantioselective modifications of the aminoacid molecule by various enzymes.

The first attempts at the employment of living organisms for the separation of aminoacid racemates were based on the ability of animals to assimilar only one optical isomer. When an animal was fed or administered a racemic aminoacid, the D-enantiomer, which had not been assimilated, could be isolated from its urine[9,10]. Despite its evident disadvantages (the permanent loss of half of the starting material, the difficulty of isolating the product from a mixture containing a whole series of all possible organic compounds, and the consequent formation of the aminoacid D-enantiomer which is usually physiologically less active and hence less valuable), this method has still not lost its importance. Thus a patent was taken out in 1976 in Japan for the preparation of D-aminoacids and their esters by treating the racemic aminoacid with the cells of the micro-organisms *Mycoplasma*, *Protaminobacter*, *Acetobacter*, *Pseudomonas*, *Aeromonas*, *Xanthomonas*, and *Bacillus*[11]. As a result of this procedure,

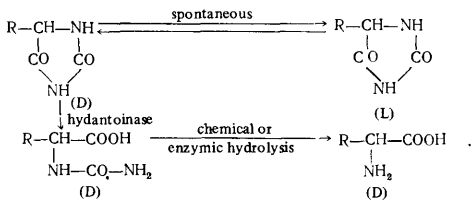
the L-isomer was assimilated by the bacteria, while the D-isomer was isolated from the culture medium after separating the cells by centrifugation.

A much greater success was achieved by employing separate enzyme preparations purified to different extents. In this case only one chemical reaction takes place and it is possible to isolate both aminoacid enantiomers. At the present time all enzymic methods for the resolution of aminoacid racemates can be divided into the following groups, which are listed in order of their increasing practical value and the extent to which they are used: (1) specific methods for the resolution of racemates suitable only for individual aminoacids (lysine, cysteine, and aromatic aminoacids); (2) stereoselective oxidation and decarboxylation of aminoacids; (3) enantioselective synthesis of the amide bond; (4) stereoselective hydrolysis of aminoacid amides and esters; (5) enantioselective hydrolysis of *N*-acylated aminoacids.

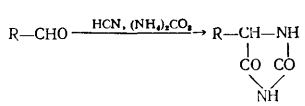
II. ENZYMIC CONVERSION OF CYCLIC AMINOACID DERIVATIVES

1. 5-Substituted Hydantoins

When enzymes are used for the resolution of aminoacid racemates into optical isomers, the problem of the utilisation of the enantiomer which has not reacted arises. It is usually solved by its chemical racemisation and the return of the resulting racemate to the resolution process. However, in the case of hydantoin derivatives of aminoacids the racemisation takes place spontaneously at fairly high rates even under the conditions of enzymic enantioselective hydrolysis. Thus the half-racemisation time of 5-phenylhydantoin at pH 8.5 and 30 °C in 0.25 M solution is 19 min[12]. This made it possible to put forward the following scheme for the enzymic resolution of aminoacid racemates using hydantoinase (dihydropyrimidinase, EC 3.5.2.2) which hydrolyses 5-substituted D-hydantoins stereoselectively:



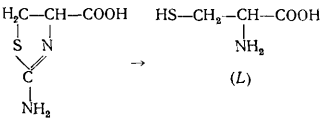
Although the formation of *N*-carbamoylaminoacids from hydantoins in the organism was observed in 1926 [13] and the possibility of the enzymic resolution of racemates was demonstrated as early as 1930,[14] the preparation of optically active aminoacids by this procedure has acquired practical importance only recently. 5-Substituted DL-hydantoins can be synthesised in a single stage from the corresponding aldehydes by the Bucherer reaction[15]:



Calf liver dihydropyrimidinase cleaves the ring of dihydropyrimidines with formation of *N*-carbamoyl-β-aminoacids[16] and is identical with the enzyme which converts hydantoin into *N*-carbamoylglycine[17]. It is of interest to note that the opening of the dihydropyrimidine or hydantoin ring is a reversible process and that the reverse reaction can be achieved under acid conditions[16,18]. The bovine liver hydantoinase catalyses the enantioselective hydrolysis of D-hydantoin derivatives of α-aminophenylacetic α-amino-*p*-chlorophenylacetic acids, leucine, alanine, methionine, and valine. The D-derivatives of glutamic and aspartic acids and tryptophan are resistant to the action of the enzyme[12,19]. Hydantoinase has been found in a whole series of microorganisms: *Klebsiella*, *Corynebacterium*, *Agrobacterium*, *Pseudomonas*, and *Bacillus*[20]. The strain *Pseudomonas striata* IFO 12 996 has proved most suitable for practical applications. The hydantoinase is induced by DL-5-methylhydantoin (a hydantoin derivative of alanine). Other hydantoins are inert or actually suppress the biosynthesis of the enzyme[21]. The hydantoinase from *Ps. striata* was purified to a homogeneous state and was obtained in a crystalline form. Its molecular weight is 190 000 and it consists of four identical subunits[22]. Tables 1 and 2 indicate the substrate specificity of the hydantoinase from *Ps. striata*. 5,5-Disubstituted hydantoins are not cleaved by the enzyme. The hydantoinase from *Corynebacterium sepedonicum* and *Aerobacter cloacae* differs somewhat in its substrate specificity from the enzyme obtained from *Ps. striata*[23]. Thus the best substrate for the latter is DL-5-*m*-chlorophenylhydantoin, while for the former the best substrate is DL-5-*p*-chlorophenylhydantoin. A hydantoinase which effectively hydrolyses the hydantoin derivatives of various substituted 5-phenylhydantoins, particularly 5-thienylhydantoin, has been isolated from the micro-organisms *Bacillus sp.* 121-3.[24,25] The strains of the soil micro-organisms T-524, T-639, and especially T-523 effectively convert 4,5-indolylmethylhydantoin into tryptophan, exhibiting not only the hydantoinase but also the N-carbamoylhydrolase activity. The optical purity of the L-tryptophan obtained in this way from the racemic hydantoin reaches 99.1%.[26] L-Glutamic acid can be obtained from DL-5-β-carboxyethylhydantoin with the acid of the micro-organism *Bacillus brevis* ATCC 8185. When it is cultured in a weakly alkaline medium containing 1.0% of DL-5-β-carboxyethylhydantoin, it is possible to convert 90% of the racemate into L-glutamic acid. The enzyme system responsible for this reaction is induced by the addition of the initial substrate to the medium[27]. A reactor capable of processing up to 3 kg of hydantoin per day has been devised on the basis of calf liver hydantoinase incorporated in triacetate fibres. The half-life of the catalyst at pH 8.5 at 30 °C was 20 days[12].

2. 2-Amino-Δ^2-thiazoline-4-carboxylic Acid

L-Cysteine can be obtained from DL-2-amino-Δ^2-thiazoline-4-carboxylic acid using *Pseudomonas* cells[28]:



The reaction yield is close to 100% because the hydrolysis of the thiazoline ring of the L-isomer is accompanied by the racemisation of the D-enantiomer of the substrate in the reaction mixture. The strain *Pseudomonas thiazolinophylum* AI3854 showed the highest activity among the 463 strains of the 37 species tested. The enzyme (or enzyme system) responsible for the conversion is an induced intracellular enzyme closely associated with cell growth. Further degradation of cysteine (or cystine) can be prevented by introducing hydroxylamine or semicarbazide into the reaction medium and inhibiting thereby the pyridoxal 5'-phosphate-dependent cysteine desulphhydrase. The addition of Mn^{2+} (5 mM) and Fe^{2+} (25 mM) ions increases the overall activity of the enzyme

system by a factor of 5–7 and in addition the presence of Mn^{2+} ions at a concentration of 1–10 mM has a stabilising effect on the activity. When intact cells of *P. thiazolinophylum* AI3854 were used, a sigmoid time variation of the accumulation of L-cysteine was observed, but treatment of the cells with ultrasound eliminated this effect and led to a linear relation[29].

Table 1. The substrate specificity of the hydantoinase from *Ps. striata*[20].

D-substrate 

R	Relative rate of hydrolysis*	R	Relative rate of hydrolysis*
H	13	*p*-HO—C_6H_4	16
CH_3	45	*m*-HO—C_6H_4	5
$(CH_3)_2CH$	15	*p*-Cl—C_6H_4	19
CH_3—S—CH_2—CH_2	48	*m*-Cl—C_6H_4	10
$(CH_3)_2CH$—CH_2	48	*p*-CH_3O—C_6H_4	7
C_6H_5	25		

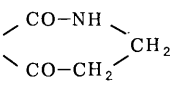
*The rate of cleavage of dihydrouracil  was adopted as 100.

Table 2. Kinetic properties of the hydantoinase from *Ps. striata*[21].

Substrate	K_M^*, mM	pH optimum of activity
Dihydrouracil	1.7	8.8–9.0
DL-5(2-Methylthioethyl)hydantoin	28	8.3–8.5
DL-5-Phenylhydantoin	50	8.0–8.3
Hydantoin	280	8.0–8.3

*K_M = Michaelis constant.

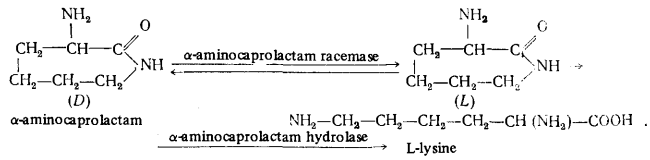
Table 3. The equilibrium constants of the hydrolysis of *N*-acetyl derivatives of aminoacids (25 °C; pH 7.5).[126]

Aminoacid	K_{eq}, hydrolysis*	K_{eq}, synthesis*
Glycine	4.0±1.5	5±1
Alanine	5.4±0.5	5.9±0.7
Aminobutyric acid	5.1±0.6	6±1
Norvaline	11±1	10±1
Norleucine	13±2	12±2

*Path followed by equilibration.

3. α-Aminocaprolactam

A very promising method of preparation of L-lysine from DL-α-aminocaprolactam (DL-ACL), proposed by the Japanese company Torrei Industries[30,31], is based on the use of the L-aminocaprolactam hydrolase–α-aminocaprolactam racemase two-enzyme system:



Caprolactamase has been isolated from various micro-organisms: *Bacillus circulans, Bacillus firmas*[32], *Cryptococcus laurentii, Candida humicola, Trichosporon cutaneum, Achromobacter cycloclastes, Achromobacter obae, Flavobacterium arborescens*, and *Alcaligenes faecalis*[33,34]. The strains of *Cryptococcus laurentii, Candida humicola*, and *Trichosporon cutaneum*, whose properties have in fact been studied in detail, proved to be the most promising[35]. Caprolactamase was purified to a homogeneous state. The enzyme consists of two subunits with a molecular weight of 67 000, a sedimentation constant of 4.4 S, and an isoelectric point $pI = 5.7$.[36,37] Caprolactamase is a metalloenzyme and its activity is fully suppressed in the presence of 7 mM *o*-phenanthroline but can be restored in the presence of Mg^{2+}, Mn^{2+}, or Zn^{2+} ions (but not Co^{2+} and Ni^{2+}) up to 30–70% of the initial value[31,37]. At pH 8.5 and 37 °C the catalytic constant of the enzyme hydrolysis of L-α-aminocaprolactam is 750 s^{-1}.[31] The enzyme hydrolyses L-α-amino-δ-valerolactam three times less effectively and D-α-amino-ε-caprolactam twenty times less effectively than L-α-aminocaprolactam and does not exhibit activity in relation to γ-butyrolactam, δ-valerolactam, ε-caprolactam, cyclic oligomers of ε-caprolactam, α,α-dichloro-ε-caprolactam, and DL-pyrrolidinone carboxylic acid[30]. Caprolactamase has recently been found to show activity in relation to L-lysinamide which is hydrolysed by the enzyme twice less effectively than L-α-aminocaprolactam[36,37]. The Michaelis constant for the hydrolysis of L-α-aminocaprolactam is 2.6 mM and that for the hydrolysis of L-lysinamide is 14 mM.[37] At high substrate concentrations the enzyme is inhibited both by the substrate and by the L-lysine formed. The reaction can be described by the equation[39]

$$\frac{d[S]}{dt} = \frac{k_{cat}[E][S]}{\left(K_M + [S] + \frac{[S]^2}{K_S}\right)\left(1 + \frac{[P]}{K_i}\right)} ,$$

where E, S, and P are respectively caprolactamase, L-α-aminocaprolactam, and L-lysine, $K_M = 0.023$ M, the substrate inhibition constant $K_S = 1.54$ M, and the product inhibition constant $K_i = 3.23$ M.

By selecting micro-organisms capable of growing on media containing only L- or D-α-aminocaprolactam as the only source of nitrogen and the main source of carbon, micro-organisms producing α-amino-ε-caprolactam racemase were selected: *Achromobacter obae, Achromobacter cycloclastes, Alcaligenes faecalis*, and *Flavobacterium arborescens*. The *Achromobacter obae* strain showed the highest activity[30]. The racemase was isolated and partly purified. Its molecular weight was 54 000 and the pH optimum of its activity was 7.5–9.0. The activity of the racemase is fully inhibited by hydroxylamine (10^{-4} M), but is restored following the addition of pyridoxal 5′-phosphate. At higher concentrations (>10^{-4} M) pyridoxal 5′-phosphate is a racemisation inhibitor[40]. Substrate inhibition is characteristic of the racemisation reaction catalysed by lyophilised cells. In addition L-lysine, inevitably present when the hydrolysis of L-α-aminocaprolactam and the racemisation of D-α-aminocaprolactam are carried out in a single reactor, is a powerful non-competitive inhibitor of this reaction. In the real process one must take into account also the inactivation of the racemase in the course of the reaction[39].

The optimum process pH depends on the ratio of the catalytic amounts of racemase and caprolactamase and shifts towards the pH optimum of the enzyme limiting the rate of the entire process. For a periodic reactor, in which the enzyme ratio can be varied during the process, the principal characteristic is the ratio

$$f = \frac{[\text{racemase}]}{[\text{racemase}] + [\text{caprolactamse}]} \quad (0 \leqslant f \leqslant 1) \ .$$

If the concentration is expressed in mole fractions, and k_1 and k_2 are the rate constants for the racemisation and hydrolytic reactions, then the composition of the reaction medium as a function of time can be described by the following system of equations:

$$\frac{d[D\text{-ACL}]}{dt} = fk_1([L\text{-ACL}] - [D\text{-ACL}]);$$

$$\frac{d[L\text{-ACL}]}{dt} = fk_1([D\text{-ACL}] - [L\text{-ACL}]) - (1-f)k_2[L\text{-ACL}];$$

$$[L\text{-ACL}]_0 = [D\text{-ACL}]_0 = 0.5 \ .$$

Initially the optimum condition is that the processes occur at $f = 0$, i.e. when the racemase is absent. Subsequently the optimum condition involves the occurrence of the reaction when [D-ACL]/[L-ACL] = 1 + α, where $\alpha = (k_2/k_1)^{1/2}$. Under these conditions, the optimum enzyme ratio is defined by the expression

$$f = \frac{\alpha(1+\alpha)}{1+(1+\alpha)^2} \ .$$

The optimum composition of the biocatalyst depends only on the ratio α. If the latter remains constant during the reaction, the process can be carried out by the optimum procedure[39].

III. ENANTIOSELECTIVE OXIDATION AND DECARBOXYLATION

Strictly speaking the enantioselective oxidation and decarboxylation of aminoacids does not constitute the resolution of aminoacid racemates because such reactions lead to the loss of half of the starting material. This is the reason why these methods have not found extensive application in the preparation of aminoacid enantiomers from their racemates.

As early as the beginning of this century, it was possible to obtain 60–70% yields of the D-isomers of alanine, leucine, valine[41], norvaline, serine, phenylalanine[42], alloisoleucine, glutamic acid, and histidine[43] by treating the aminoacid racemates with yeast, whose action was due to its decarboxylases. Later this method was employed to obtain the D-isomers (of methionine with the aid of *Proteus vulgaris*[44] and of glutamic acid[45] and lysine[46] with the aid of *E.coli* and *Bacillus cadaveris* respectively). On the other hand, the monoaminodicarboxylic acid decarboxylase, specific exclusively to the D-enantiomers and isolated from *Aspergillus ustus*, makes it possible to obtain their L-enantiomers[47].

The stereoselective oxidation of aminoacids by means of the D-aminoacid oxidase from mammalian kidneys and the L-aminoacid oxidase from snake venom has found a somewhat more extensive application:

$$\text{aminoacid racemate} + O_2 \xrightarrow{\text{oxidase}} \text{unreacted optical isomer} + \alpha\text{-ketoacid} + H_2O_2 + NH_3.$$

The L-enantiomers of alanine, methionine[48], and proline[49] were obtained by treating their racemates with D-aminoacid oxidase.

The possibility of obtaining aminoacid D-enantiomers by treating the racemates with snake venom L-aminoacid oxidase is limited by the specificity of the enzyme. Thus L-threonine, L-proline, L-alanine, L-lysine, and L-ornithine are resistant to the action of the oxidase from *Crotalus adamentus*[50,51]. However, L-alanine is readily oxidised by the enzyme from the venom of *V. libetina*[52] and L-lysine is oxidised by the enzyme from the venom of *Bothrops atrox*[53]. The acylation of the ω-amino-groups of L-lysine, L-ornithine, and L-citrulline also renders them susceptible to oxidation by the enzyme from the venom of *Crotalus adamentus*[50,51]. The reaction products do not inhibit L-aminoacid oxidase, but the α-ketoacids obtained in the oxidation of aromatic aminoacids inhibit D-aminoacid oxidase. The addition of cyanide to the reaction mixture inhibits the catalase usually present as an admixture in preparations of D-aminoacid oxidase. The hydrogen peroxide formed during the reaction under these conditions is no longer decomposed by catalase and is consumed in the oxidation of the α-ketoacid to its nearest lower aliphatic acid homologues, which are much weaker inhibitors of the D-aminoacid oxidase[53].

The ease with which the reaction can be monitored from the evolution of ammonia or the peroxide and also the exceptionally low affinity of oxidases for the uncleaved isomer makes it possible to employ stereoselective oxidation as a method for the analysis of the optical purity of aminoacid stereoisomers. By means of this procedure, it is possible to determine 0.1–0.01% of the admixture of the other isomer[54,55].

The resolution of racemates by stereoselective oxidation and also by stereoselective decarboxylation has not found extensive application, firstly owing to the loss of half of the starting material in the reaction and, secondly, owing to the high cost of snake venom—the source of L-aminoacid oxidase.

IV. ENZYMIC SYNTHESIS OF THE AMIDE BOND

An interesting method for the resolution of aminoacid racemates is the enantioselective synthesis of the amide linkage catalysed by various proteolytic enzymes. It is well known that the hydrolysis of the amide linkage formed by *N*-acylated aminoacid derivatives proceeds until the attainment of equilibrium and under certain conditions the reverse synthetic reaction can be achieved[56–58]. If aniline or phenylhydrazine is used as the amino-group donor for the synthesis of the amide linkage, then the anilides or phenylhydrazides of the *N*-acylated aminoacids, which are sparingly soluble in water and crystallise from the reaction mixture, are formed as a rule. This shifts the equilibrium in the direction of synthesis and makes it possible to carry out the stereoselective synthesis almost quantitatively. Attention was drawn to the enantioselectivity of such synthesis, catalysed by papain, for the first time in a study of the synthesis of acetyl-DL-phenylalanylglycine anilide[58].

A similar method was used to resolve the racemate in benzyloxycarbonyl-DL-glutamic acid[59] and the diastereoisomer of acetyl-DL-phenylalanyl-L-leucine[60]. Later the method was improved[61] and it was possible to resolve by this procedure the racemates of alanine, leucine, isoleucine, norleucine, valine, lysine, serine, threonine, and phenylalanine.

For the synthesis reaction of the anilide to go almost to completion, the *N*-acylaminoacid must be readily soluble and the corresponding anilide must be sparingly soluble. The choice of a suitable *N*-acyl group on the grounds of solubility can entail in its turn difficulties associated with the stereospecificity of the enzyme employed[60]. This question was investigated in greater detail in relation to the papain-catalysed stereoselective synthesis of the phenylhydrazides of *N*-acylated aminoacids[62–64]. The replacement of aniline by phenylhydrazine is dictated by the fact that the phenylhydrazide group can be readily removed by mild oxidation.

The product synthesised was found to have almost fully the *L*-configuration if the acyl group was acetyl or benzoyl. If the acyl group consisted of methoxycarbonyl, ethoxycarbonyl, or benzyloxycarbonyl residues, then a considerable amount of the D-hydrazide, almost comparable to the amount of the L-hydrazide, was formed. This phenomenon was observed regardless of the nature of the aminoacid residue, although the rate of formation of the product is influenced by the nature of both the *N*-acyl group and of the slight change of the aminoacid itself[65-67]. Unfortunately quantitative conclusions as regards this system are hindered by the continuous inactivation of papain by phenylhydrazine[63].

Despite a number of evident advantages, namely the simplicity of the enantioselective synthesis of the anilide or phenylhydrazide and the exceptionally convenient separation of the unreacted D-isomer, this method has not found extensive applications for the resolution of aminoacid racemates into optical isomers and its possible comparative use has been pointed out in only isolated studies[68]. This is associated, firstly, with the difficulty of choosing a suitable acyl derivative of the aminoacid satisfying all the essential requirements, secondly, with the necessity for a careful selection and constant monitoring of the conditions in the resolution process, and, thirdly, with the fact that the starting materials and the reaction products are not aminoacids themselves but fairly complex derivatives of the latter. This necessitates additional synthetic stages followed by the hydrolysis of these compounds. Since the anilides of the acylated aminoacids are fairly stable, refluxing for many hours in 6 M HCl must be used for the preparation of the free aminoacid[59]. This is why, even if the L-compound does not contain initially admixtures of the other isomers, such treatment can lead to partial racemisation[66,69] and in the case of certain aminoacids, for example, methionine[70] and tryptophan[71], to chemical degradation.

Despite the fact that the stereoselective synthesis catalysed by various proteolytic enzymes is hardly used for the resolution of aminoacid racemates into optical isomers, reactions of this type are being vigorously investigated. They have already found applications in the stereoselective synthesis of various *N*-acylated oligopeptides. Apart from papain, the synthesis of the amide linkage can be catalysed by α-chymotrypsin[72], nagarase, pepsin, and thermolysin[73]. The employment of proteolytic enzymes with different specificities makes it possible to incorporate various aminoacids in the oligopeptides synthesised. The kinetics of both the direct synthesis of the amide linkage, for example, the papain-catalysed synthesis of hippurylanilide from aniline and hyppuric acid[74] as well as the formation of the dipeptide from *N*-benzoyl-L-tyrosine and glycineanilide catalysed by α-chymotrypsin[75], and the "synthesis with transfer", where instead of the *N*-acylated aminoacid one uses its more reactive derivative, usually the ester, as the carboxyl donor for the formation of the amide linkage, have been studied in detail. Proteolytic enzymes such as trypsin[76] and α-chymotrypsin[77] are catalysts of reactions of this kind. Since the hydrolysis of amide and ester substrates of these enzymes proceeds via the formation of the acyl-enzyme, it follows that, in accordance with the principle of microreversibility, the synthesis should also proceed via these intermediate states. The use of aminoacid esters as donors of the carboxy-group facilitates the acylation stage compared with the acylation of the free aminoacid, which accelerates the entire process, because the deacylation stage is not rate-limiting[78], and makes it possible to use aminoacid esters with a free amino-group as donors of the carboxy-group[79]. Furthermore, for a specific ratio of the kinetic parameters of the hydrolytic and synthetic reactions, it is possible to achieve yields exceeds the thermodynamic values in "synthesis with transfer"[80,81].

The study of the equilibrium constants of the hydrolytic-synthetic reactions of the amide or peptide linkage[82-85] permitted the conclusion that the free energy of the synthesis, calculated in relation to the unionised forms of the starting materials and reaction products, is as a rule negative, i.e. the equilibrium is displaced towards synthesis. However, when the reactions are carried out in aqueous solutions, the vast majority of one or both starting materials exist in the ionised form (since the p*K* of the carboxy-groups of such compounds are in the range 2–3.5 and the p*K* of the amino-groups are in the range 6–9.5) and the synthesis of the amide and peptide linkages is no longer such a thermodynamically favourable process[56,57].

Various methods whereby the reaction equilibrium can be displaced towards the required product have been vigorously developed recently[86-88]. Such methods are based on the alteration of the ionisation constants of the reactants and the decrease of the concentration of water in the system, the employment of two-phase "water–water-immiscible organic solvent" systems, or the creation of conditions for a kinetically controlled equilibrium as a result of the immobilisation of the enzyme on a charged carrier. Admittedly this entails an appreciable decrease of the rate of synthesis and additional components, hindering the isolation of the required product, are introduced into the system.

Summarising, one may say that, although the stereoselective method of synthesis of amides, hydrazides, or peptides under the influence of proteolytic enzymes has not found applications as a procedure for the resolution of aminoacid racemates into optical isomers, the study of such reactions has made it possible to understand many features of the thermodynamics of the important reaction involving the synthesis of the peptide linkage and provided synthetic chemists with a convenient method whereby one can synthesise various oligopeptides stereoselectively under mild conditions and with a high yield[89-91].

V. ENANTIOSELECTIVE HYDROLYSIS OF AMINOACID ESTERS AND AMIDES

The stereoselective hydrolysis of aminoacid esters was first used for the resolution of racemates into optical isomers in 1906,[92] i.e. it was contemporary with the classical diastereoisomeric crystallisation methods. A common disadvantage of the method described was the long time involved and their laborious nature, since the employment of low-purity enzyme preparations required much time for the hydrolytic reaction and led to contamination by products of side reactions.

Despite these difficulties, tryptophan[93-97], phenylalanine[98-100], norleucine[100], methionine[94], valine[98,99], and a number of benzene ring-substituted phenylalanine[98,99,101,102] racemates have been resolved by the stereoselective hydrolysis of their esters under the influence of pancreatic enzymes.

The studies discussed above were extremely empirical. The isolation of proteolytic pancreatic enzymes in a pure form, the discovery and isolation of numerous proteases from various micro-organisms, and the development of a convenient method whereby the kinetics of reactions of this kind can be followed (pH-stat measurements) renewed the interest in the stereoselective hydrolysis of esters as a method for the resolution of aminoacid racemates into optical isomers.

1. Characteristics of the Action of α-Chymotrypsin on Aminoacid Esters

Despite the fact that α-chymotrypsin is one of the most thoroughly investigated enzymes[103], the mechanism of the hydrolysis by the latter of aminoacid esters has not been

ultimately elucidated. As for the esters of *N*-acylated amino-acids, the formation of an intermediate acyl-enzyme has been postulated in all the investigations for esters with a free amino-group, but the question which stage, acylation or deacylation, is rate-limiting still remains open[104–109].

The hypothesis that in the hydrolysis of aminoacid esters by α-chymotrypsin the reactive form of the Michaelis complex is a complex of the enzyme with the substrate protonated in the amino-group can now be regarded as having been convincingly demonstrated[104,105,109–112]. It is supported by the higher reactivity in hydrolytic reactions of the forms of aminoacid esters protonated in the amino-group[113] and also by the possibility of the formation of a hydrogen bond between the NH_3^+ group and the carbonyl group of Ser[214,112]. The formation of a hydrogen bond in the Michaelis complex would ensure a more favourable binding of the substrate and, in accordance with the "better binding–better catalysis" principle[103], might occur in the catalytic stage of the chymotrypsin catalysis. The results of the crystallographic study of α-chymotrypsin indicate the presence in the active centre of the enzyme, alongside the hydrophobic section, of the aspartic acid residue Asp[194], participating in the formation of a salt bridge, which is necessary for the maintenance of the catalytically active tertiary structure[114,115] and is capable of electrostatic interaction with the protonated amino-group of the substrate. The mechanism of the enzymic (chymotrypsin) hydrolysis of aminoacid esters with a free amino-group, proposed on the basis of these considerations, describes satisfactorily the pH dependence of all the kinetic parameters[109].

A characteristic property of α-chymotrypsin is its high stereospecificity with respect to the L-isomers of aminoacid esters with a free amino-group, which makes it possible to use this reaction for the separation of aminoacid racemates. It is of interest to examine factors determining the high stereospecificity of α-chymotrypsin. The idea that the stereospecificity is determined by the structure of the substrate and is not an invariant property of the enzyme has been confirmed in the study of the hydrolysis of the *p*-nitrophenyl esters of *N*-acetylated aminoacids[116,117]. As the side chains of the substrate becomes more hydrophobic, the deacylation of the L-acyl-enzymes is accelerated, while that of the corresponding D-acyl-enzymes is retarded.

According to the view which has become firmly established at the present time[103], the driving force of the chymotrypsin catalysis is the hydrophobic interaction between the side chain (R^2) of the substrate having the general formula $R^2–CH(NHR^1)–COR^3$ and the groups located in the hydrophobic region of the active centre of the enzyme. The "better binding–better catalysis" rule is then observed. However, it is applicable only to the variation of R^2. It has been shown[118] that, when the *N*-acyl group in ester derivatives of L-aniline is altered, the "better binding–less effective reaction" relation is observed. In order to interpret this effect, the hypothesis of the "unproductive binding" of the substrate molecule by the enzyme was put forward. The binding of the molecules of the L- and D-substrates can be illustrated schematically on the basis of the model involving the three-point binding of the substrate to the active centre of α-chymotrypsin (Fig. 1). Evidently in the case of the L-substrate the "correct" binding is at the same time also productive. Therefore the enhancement of the hydrophobic properties of the aminoacid side chain (the group R^2) leads to an increase of the efficiency of the catalysis (Fig. 1*a*). The unproductive binding can be explained in this instance by the fact that the *N*-acyl group R^1, which is fairly hydrophobic, can itself occupy a site in the hydrophobic section of the active centre and the carbonyl group attached to the bond undergoing dissociation in the substrate will not be correctly oriented in relation to the general nucleophile of the active centre (Fig. 1*b*).

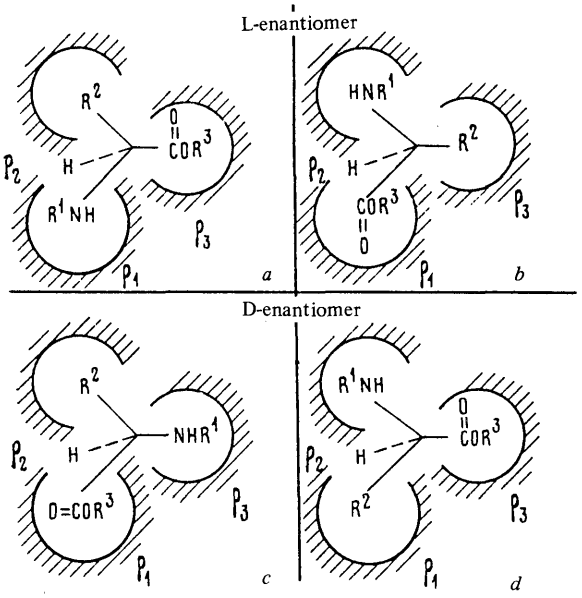


Figure 1. Different versions of the three-point binding of the substrate molecule to the active centre of α-chymotrypsin; ρ_1 = hydrogen bond acceptor; ρ_2 = hydrophobic region of the active centre; ρ_3 = generalised nucleophile of the active centre.

The hydrolysis of D-aminoacid derivatives takes place in exactly the opposite manner: the "correct" binding of the substrate, i.e. binding such that the group R^2 is in the hydrophobic section of the active centre, leads to an unproductive enzyme–substrate complex (Fig. 1*c*), since the formation of the productive complex is in this case sterically hindered and requires that the *N*-acylamide group occupy the site provided in the active centre for the hydrogen centre[119]. On the other hand, the "incorrect" orientation of the *N*-acylamide group in the hydrophobic region ρ_2 is in fact productive (Fig. 1*d*). It is clear from the foregoing that the enhancement of the hydrophobic properties of the aminoacid group R^2 entails an increase of the stereospecificity of the enzyme, while the enhancement of the hydrophobic properties of the *N*-acyl group R^1 should actually reduce it. This conclusion has been confirmed experimentally[120,121].

For the resolution of aminoacid racemates, it is important to know how the stereospecificity of the action of α-chymotrypsin changes on passing to substrates with a free amino-group. It was found that the character of the influence of the hydrophobic properties of the group R^2 on the stereospecificity of the chymotrypsin hydrolysis of the methyl esters of aminoacids is the same for substrates with free and acetylated amino-groups, but the ratio of the second-order rate constants for the enzyme hydrolysis of L- and D-substrates is approximately 10 times greater for acetylated aminoacids than for aminoacids with a free amino-group. The

D-substrate having a free amino-group is hydrolysed by α-chymotrypsin faster than its acylated analogue[112].

2. The Problem of the Spontaneous Hydrolysis of α-Aminoacid Esters

In the stereoselective hydrolysis of aminoacid esters by proteolytic enzymes the spontaneous (non-enzymic) hydrolysis of the aminoacid esters is one of the concomitant processes interfering with the effective resolution of their racemic mixture. It is therefore necessary to seek optimum conditions which correspond both to relatively low rates of spontaneous hydrolysis and to an adequate activity of the biocatalyst employed. The most sensitive parameters of such optimisation are the pH of the solution and the reaction temperature. It is therefore very urgently necessary to compare the pH profile of the catalytic activity of the enzyme and the pH dependence of the rate of spontaneous hydrolysis.

Until recently, the hydrolysis of aminoacid esters has been studied only over a narrow range of alkaline pH (9–12), which did not allow the estimation of the rate of the process in neutral and weakly acid media[122–125]. The following kinetic mechanism has been proposed on the basis of a detailed study of the pH dependence of the hydrolysis of the ethyl ester of DL-tryptophan in the pH range 4.5–10.5:[113]

$$\left.\begin{array}{l}\xleftarrow{k_5[OH^-]}\\ \xleftarrow{k_3[H_2O]}\end{array}\right| -EH^+ \overset{K_E}{\rightleftharpoons} E- \left|\begin{array}{l}\xrightarrow{k_1[H^+]}\ ,\\ \xrightarrow{k_2[H_2O]}\ ,\\ \xrightarrow{k_4[OH^-]}\ ,\end{array}\right. \qquad (1)$$

together with the corresponding equation for the rate of hydrolysis:

$$V = k_1[E][H^+] + k_2[E][H_2O] + k_3[EH^+][H_2O] + k_4[E][OH^-] + k_5[EH^+][OH^-] = k_{abs}[E]_{tot},$$

where EH^+ and E are the form of the aminoacid ester protonated in the amino-group and the non-protonated form and k_1, k_2, k_3, k_4, and k_5 are the rate constants for the acid, neutral, and alkaline hydrolysis. The possibility of the acid hydrolysis of the protonated form of the substrate, which is unlikely in view of the electrostatic repulsion of the interacting species, is not reflected in mechanism (1). Analysis of the pH dependence of k_{obs} obtained and the literature data for the hydrolysis of *N*-acylated aminoacid esters made it possible to find or at least to estimate all the kinetic parameters of mechanism (1):

$$k_1 \cong 10^{-5} \text{ litre mol}^{-1}\text{s}^{-1},\ k_2 \cong 10^{-7} \text{ litre mol}^{-1}\text{s}^{-1},\ k_3 = 2.7 \times 10^{-7} \text{ litre mol}^{-1}\text{s}^{-1},$$
$$k_4 = 1.2 \text{ litre mol}^{-1}\text{s}^{-1},\ k_5 = 79 \text{ litre mol}^{-1}\text{s}^{-1}.$$

The pH dependence of the hydrolysis of the ethyl ester of DL-tryptophan permits certain practically important solutions. Thus, in order to diminish the contribution of the spontaneous hydrolysis as a side process in the enzymic resolution of aminoacid racemates as a result of the stereoselective hydrolysis of their esters, it is necessary to employ proteolytic enzymes with a pH optimum of the catalytic activity in the region of acid and neutral pH (neutral and acid proteases). The possibility of employing alkaline proteases is to a large extent limited, because in the region of the alkaline pH the rate of spontaneous hydrolysis is so high that it is difficult to avoid the contamination of the final product even when high enzyme concentrations are used and the process is carried out over a short time interval.

In the study of the possibility of employing a particular proteolytic enzyme for the resolution of aminoacid racemates by the enantioselective hydrolysis of aminoacid esters, it is important to know the characteristics of the reaction at substrate concentrations close to saturation, i.e. under the conditions of the preparative resolution of aminoacid racemates. It has been shown[126,127] that the full kinetic curves for the enantioselective hydrolysis of the ethyl ester of DL-tryptophan, catalysed by α-chymotrypsin, are described by the mechanism

$$E\cdot D\text{-}S \overset{K_i'}{\rightleftharpoons} D\text{-}S + E + L\text{-}S \overset{K_S}{\rightleftharpoons} E\cdot L\text{-}S \xrightarrow{k_2} EA \xrightarrow{k_3} E + P,$$
$$P \quad (P' \text{ from } E\cdot L\text{-}S), \qquad E\cdot P \quad (K_i)$$

where *E* is α-chymotrypsin, L-S and D-S are the ethyl esters of L- and D-tryptophan respectively, P is L-tryptophan, P′ is ethanol, $K_i' = (1.8 \pm 0.3) \times 10^{-3}$ mol litre^{-1} is the constant of the competitive inhibition by the ethyl ester of D-tryptophan, $K_i = (25 \pm 5) \times 10^{-3}$ mol litre^{-1} is the constant of the competitive inhibition by L-tryptophan, $k_{cat} = k_2k_3/(k_2 + k_3) = 100 \pm 10$ s^{-1} is the catalytic constant, and $K_M = K_Sk_3/(k_2 + k_3) = (2.4 \pm 0.1) \times 10^{-3}$ M is the Michaelis constant (all the constants were determined at 37 °C and pH 6.3).

Summarising the discussion of α-chymotrypsin as a potential catalyst of the enantioselective hydrolysis of aromatic acid esters, one may make the following conclusions: firstly, α-chymotrypsin is highly stereospecific. Secondly, the pH optimum of the catalytic efficiency of the action of α-chymotrypsin on aminoacid esters with a free amino group is in the pH range 6.5–7.0, where the non-enzymic hydrolysis of the substrate proceeds to only an insignificant extent; the rates of the enzymic hydrolysis of the L-isomer of the substrate, of the enzymic hydrolysis of the D-isomer, and of the spontaneous hydrolysis of the racemate at the pH optimum of the α-chymotrypsin activity are approximately 10 000 : 1 : : 0.0001, which leads to a very insignificant contamination of the final product by the other isomer. Thirdly, the optimum pH range from the standpoint of the relative contributions of the enzymic and non-enzymic hydrolytic reactions is in fact also most convenient for the isolation of the reaction product from the reaction mixture, because in this particular pH range aminoacids are least soluble and the substrate hydrolysed is fairly soluble. Fourthly, L-tryptophan and ethanol, formed in the enzymic reaction, have an insignificant influence on the process kinetics, which makes it possible to achieve high degrees of conversion of the substrate.

Thus α-chymotrypsin is an exceptionally convenient catalyst for the resolution of aromatic aminoacid racemates by the hydrolysis of their esters. However, a significant disadvantage of α-chymotrypsin is its animal origin and hence its relatively high cost. A possible way of overcoming this disadvantage may be the use of immobilised preparations of the enzyme with a fairly high stability, which would make possible their repeated employment in the process. The immobilisation of α-chymotrypsin has been thoroughly investigated[6] and there is no doubt that active preparations of the immobilised enzyme with a high stability and effective mechanical properties necessary for practical applications can be obtained. Another solution of the problem is to seek proteolytic enzymes of microbial origin with properties close to those of α-chymotrypsin.

3. The Stereospecificity of Proteolytic Enzymes

Bacterial proteases have been studied only recently from the standpoint of their suitability for the resolution of aminoacid racemates[126–129]. Unfortunately, all the enzymes or

enzyme complexes of bacterial origin investigated are appreciably inferior to their activities and, what is most important, in their enantioselectivity to α-chymotrypsin. The proteases from *Bacillus subtilis* and the extracellular protease from *Actinomyces* are the most suitable for the stereoselective hydrolysis of aminoacid esters. The catalytic constants for the hydrolysis of the ethyl ester L-tryptophan at the pH optimum are 6.5 ± 0.5 and 3.2 ± 0.4 s^{-1} for these enzymes and their enantioselectivities, i.e. the ratios of the catalytic constants for the enzyme hydrolysis of the L- and D-isomers of the ethyl ester of tryptophan, are 200 and 150 respectively. For α-chymotrypsin, these quantities are 100 s^{-1} and 10 000.[126,129] Furthermore, the pH optimum of the catalytic activity of these substrates corresponds to a weakly alkaline region where the solubility of the substrate is low and the contribution of the non-enzymic hydrolysis increases.

The relatively low stereospecificity of the microbial proteolytic enzymes can be associated with the fact that contacts with the aminoacid residues, remote from the bond undergoing cleavage in the hydrolysis of oligopeptide and polypeptide substrates, are exceptionally important for such an enzyme in contrast to, say, α-chymotrypsin[130]. Thus the replacement of an acetylaminoacid amide by an oligopeptide, fully covering the active centre of the enzyme, entails an increase of the efficiency of the action of chymotrypsin by a factor of 4000,[131] of trypsin by a factor of 300,[132] and for the microbial enzymes elastase and the protease from *Streptomyces griseus*, the corresponding increase in the efficiency of hydrolysis is by a factor of 10^7.[130,133–135] Such increase of the efficiency of hydrolysis is apparently due to the stronger binding of the oligopeptide substrates compared with the acetyl aminoacid amide and hence to their more "accurate" orientation, which should lead to an increase of the stereospecificity of the action of these enzymes. However, it is entirely likely that, among the large number of microbial proteases, there is an enzyme corresponding to the highest requirements which must be met by the catalyst of the stereoselective hydrolysis of aminoacid esters for the resolution of the racemate into optical isomers, while the addition of metal ions will make it possible to increase the stereospecificity of bacterial proteases[128,136,137].

The racemates of acetyl-leucine[138], methionine, and α-aminophenylacetic acid[139] have been resolved into optical isomers by the enantioselective hydrolysis of their amides by proteolytic enzymes. However, it is important to note that the stereoselective hydrolysis of aminoacid amides has not found extensive applications owing to the low rates of hydrolysis of the amide substrates compared with the ester derivatives of aminoacids.

VI. THE USE OF ACYLAMIDOHYDROLASES FOR THE RESOLUTION OF RACEMATES

The stereoselective hydrolysis of *N*-acylated aminoacids has come to be most widely used nowadays among all the methods for the resolution of racemates. The application of this method was initiated in 1922, when it was observed that preparations of animal tissues catalyse the hydrolysis of *N*-benzoyl-L-aminoacids only[140]. Subsequently the possibility of the hydrolysis of not only benzoyl derivatives but also of other *N*-acylaminoacids was demonstrated[141–144]. Extensive practical application of the stereoselective hydrolysis of acylated aminoacids became possible only after a series of studies by Greenstein and co-workers who were able to resolve the racemates of virtually all natural and a number of synthetic aminoacids by employing a pig kidney homogenate or partly purified preparations of aminoacid acylase[145].

The enzyme catalysing the hydrolysis of *N*-acylated aminoacids has come to be called aminoacid acylase (EC 3.5.1.14). Aminoacid acylases belong to the group of enzymes hydrolysing non-peptide bonds (EC 3.5..). However, the similarity of the properties of the C–N bond in acylated aminoacids and peptides and also the necessity for a free carboxy-group for the manifestation of the acylase activity indicate that the acylase is related to a number of enzymes hydrolysing the peptide linkage (EC 3.4..), for example, carboxylpeptidases (EC 3.4.2), which split off the *C*-terminal aminoacid from peptides and are capable of hydrolysing *N*-acylated aminoacids with an aromatic side chain. Furthermore, aminoacid acylases exhibit a dipeptidase activity[146], which relates them to the group of dipeptidases (EC 3.4.3.). Such similarity of the substrate specificities of acylases and other enzymes sometimes leads to confusion. Thus in certain studies it has been suggested that the determination of the acylase activity in the liver be used for the diagnosis of virial hepatitis, although in fact this involves the monitoring of the hydrolysis of *N*-butyryl-γ-L-glutamyl-β-naphthylamide and the determination of the β-naphthylamine liberated in the reaction[147,148]. The activity determined is in fact due to an amidase (EC 3.5.1.4) and not an acylase.

Apart from acylase I, at least a further two enzymes capable of hydrolysing *N*-acylated aminoacids have been isolated from animal tissues. The first of these, catalysing the hydrolysis of acyl derivatives of aspartic acid, was called pig kidney acylase II (EC 3.5.1.15). The second enzyme, which hydrolyses *N*-acylated aromatic aminoacids (tyrosine, phenylalanine, tryptophan, and β-phenylserine) has been called acylase III.[149,150] Both these enzymes have been hardly investigated and the existence of acylase (III) has been altogether questioned and its activity has been attributed to carboxypeptidase. Only in recent years studies have been published confirming the presence of a special enzyme hydrolysing the *N*-acyl derivatives of aromatic aminoacids[151,152]. There are indications in the literature also of the presence of a special enzyme responsible for the hydrolysis of *N*-formylmethionine[153].

The biological role of acylases has not been ultimately elucidated. It has been suggested that they are involved in the catabolism of the *N*-acetylaminoacids formed in the hydrolysis of *N*-acetylated proteins[154,155].

1. The Pig Kidney Acylase

The pig kidney aminoacid acylase I has been isolated in a homogeneous state and its physical and chemical properties have been investigated[156–162]. It is a two-subunit enzyme with a molecular weight of 86 000, consisting of 772 aminoacid residues. Each enzyme subunit contains two SH groups, one of which is significantly more active with respect to various SH reagents. The modification of two SH groups per molecule of the enzyme leads to its complete inactivation. Each subunit contains two S–S bonds. The reduction of two S–S bonds per enzyme molecule also results in complete enzyme inactivation[158]. The acylase is likewise fully inactivated by the photochemical oxidation or chemical modification of four histidine residues[160] and two tryptophan residues[159] per enzyme molecule.

It has been recently reported that acylase I is a zinc-dependent metalloenzyme[161] containing one zinc atom per subunit.

Consideration of the substrate specificity of the pig kidney aminoacid acylase makes it possible to isolate two factors: (a) the specificity of the enzyme with respect to the type of aminoacid residue and (b) its specificity with respect to the nature of the acyl group.

Acylase I exhibits a fairly broad specificity and hydrolyses at a high rate the derivatives of the majority of aliphatic aminoacids[161,163]. The catalytic constant of the hydrolysis of acetyl-L-methionine at pH 7.0 and 37 °C is 330 s^{-1} (determined for an electrophoretically homogeneous enzyme)[157]. The Michaelis constants for the majority of acetyl derivatives of L-aminoacids amount to several millimoles. An increase of the chain length in the unbranched aminoacid residue entails an increase of the efficiency of the hydrolysis. If the results are expressed within the framework of the "structure–reactivity" correlation

$$\lg \frac{V_{max}}{K_M} = \alpha\pi + \text{const} \quad ,$$

where V_{max} is the maximum velocity of the enzymic reaction, K_M the Michaelis constant, π the Hansch hydrophobic constant for the substituent which is varied in the given series (π characterises the free energy of the transfer of the hydrocarbon residue from water to a standard hydrophobic phase—1-octanol, amounting to 0.51 for the CH_2 group in the unbranched substituent), and α the proportionality coefficient, it is found that the data obtained are described by a linear relation with a proportionality coefficient $\alpha \cong 0.7$. On passing from a linear aminoacid residue to a branched residue with the same number of carbon atoms (norvaline–valine, norleucine–leucine), the efficiency of the hydrolysis falls by a factor of 5–10. Thus the correlation obtained between the kinetic efficiency and the hydrophobic properties of the substrate shows that the simple "extraction" model of the utilisation of the substrate binding energy in the course of the enzymic reaction is valid for the pig kidney acylase (a detailed explanation of the model of the utilisation of the binding energy in the enzymic reaction has been given, for example, by Berezin and Martinek[103]). The hydrophobic section of the active centre of the acylase is a narrow "slit" whose length corresponds to at least four methylene units[163]. The results obtained agree with data for the inhibition of the acylase by free aminoacids[164] and with the finding that aromatic aminoacid derivatives are hydrolysed 2–3 times more slowly than methionine derivatives. The presence of electron-donating substituents in the aromatic ring of the aminoacid side chain results in a further decrease of the rate of hydrolysis[165]. Acyl derivatives of proline and hydroxyproline are resistant to the action of acylase I.[149] As regards the specificity of acylase I to the nature of the acyl component of the substrate, the enzyme hydrolyses different acyl-aminoacid derivatives. Among derivatives of unsubstituted aliphatic acids, acetylaminoacids are the best substrates[166]. The formyl and propionyl derivatives are hydrolysed less effectively than the acetyl derivatives. The appearance of electron-accepting substituents in the acyl component increases the rate of hydrolysis. The reactivity of the substrates increases in the sequence iodoacetyl < bromoacetyl < chloroacetyl < fluoroacetyl derivatives[149]. The benzoyl derivatives of aminoacids are poor substrates. The presence of electron-accepting substituents in the *para*-position in the benzoyl derivatives of aminoacids accelerates and the presence of electron-donating substituents retards the hydrolysis catalysed by acylase I.[165]

There are data showing that acylase I is capable of catalysing the hydrolysis of dipeptides[146,164,167], although the rate of hydrolysis is lower by 2–3 orders of magnitude compared with the chloroacetyl derivatives of aminoacids. It is of interest to note that the enzyme preparation investigated cleaved dipeptides with the L–L configuration but did not cleave those with the D–D and D–L configurations[146]. It was concluded that, for the manifestation of the catalytic activity of acylase I, it is essential that not only the C-terminal but also the *N*-terminal aminoacids should be in the L-configuration. At the same time, it is known that the acylase hydrolyses equally effectively both diastereoisomers of DL-α-chloropropionyl-L-alanine[167].

However, one should note that commercial preparations of acylase (I) without additional purification were used in the above investigations[146,167]. Presumably the observed activity in relation to dipeptides, which is lower by at least two orders of magnitude than the activity of acylase I in relation to *N*-acetyl-L-methionine, is a consequence of an admixture of another enzyme—a dipeptidase. Kördel and Schneider[164] used an electrophoretically homogeneous preparation of acylase (I), but in this case too the criterion of homogeneity employed can hardly guarantee the absence of less than 1% of an impurity protein. Thus the question of the dipeptidase activity of acylase (I) must be regarded as open.

It has been shown that the Michaelis constants for non-specific substrates (acetyl derivatives of aromatic aminoacids and derivatives of aliphatic aminoacids with a bulky acyl component) are approximately equal to the constants for the competitive inhibition of the hydrolysis of specific substrates in the presence of non-specific substrates[165]. If the three-stage mechanism of the enzymic reaction is valid for acylase I, then in this case such equality would imply that the rates of hydrolysis of non-specific substrates of acylase I are limited by the enzyme acylation stage[165]. However, the validity of the three-stage mechanism of the acylase-catalysed hydrolysis has not so far been in any way demonstrated.

At acid pH it has been possible to observe kinetically and with the aid of sedimentation equilibria the dissociation of acylase I into inactive subunits[168]. The dissociation constant is 2.0×10^{-7} M at pH 7.2 and 1.1×10^{-3} M at pH 5.8. The dissociation into inactive monomers under the influence of the substrate explains the substrate inhibition of the activity of acylase I at acid pH and the fact that there is a "flash" on the product accumulation curve under these conditions[168,165].

The pH optimum of the catalytic activity is in the pH range 7.0–7.5.[164] The Michaelis constant for the hydrolysis of acetyl-L-methionine catalysed by acylase I is independent of pH and the pH dependence of the maximum rate is bell-shaped and can be described in terms of the ionisation of two ionogenic groups having $pK_a = 6.7$ and $pK_b = 8.9$.[170]

One should note that, in the presence of high concentrations of the product of the hydrolytic reaction catalysed by acylase I, namely the acetate ion and the aminoacid, the hydrolysis of *N*-acetylaminoacids proceeds only as far as the attainment of equilibrium in the system and does not go to completion[171–173]. However, only qualitative data were available until recently for the kinetics of the synthesis of *N*-acetyl derivatives of aminoacids catalysed by the pig kidney acylase I.

2. Kinetic and Thermodynamic Characteristics of the Action of Acylase

The application to the study of acylases of a recently developed method for the quantitative determination of aminoacids, based on the spectrophotometric measurement of the product of the interaction of the aminoacid with *o*-phthalaldehyde in the presence of mercaptoethanol[177], permitted a detailed investigation of the kinetics of the hydrolysis-synthesis of acetyl-L-methionine catalysed by the pig kidney acylase I and made it possible to put forward a kinetic mechanism of the action of the enzyme and to determine the

kinetic parameters of the reaction[126,170,178]:

$$E + S \underset{}{\overset{K_M}{\rightleftharpoons}} ES \underset{V_{synth}}{\overset{V_{hydr}}{\rightleftharpoons}} EPP' \leftarrow \left[\begin{array}{l} \xrightarrow{K'_M} EP + P' \xleftarrow{K_i} \\ \xrightarrow{} EP' + P \longleftarrow \end{array} \right] \rightarrow E + P + P' \quad (2)$$

where E is the acylase, S is acetyl-L-methionine, P is sodium acetate, P' is L-methionine, $K_M = (25 \pm 3) \times 10^{-3}$ M and $K'_M = (140 \pm 20) \times 10^{-3}$ M are the Michaelis constants for the hydrolytic synthetic reactions respectively, $K_i = (43 \pm 5) \times 10^{-3}$ M is the acetate ion binding constant, and $V_{hydr} = (17 \pm 2) \times 10^{-5}$ mol litre^{-1} s^{-1} and $V_{synth} = (2.1 \pm 0.3) \times 10^{-5}$ mol litre^{-1} s^{-1} are the maximum rates of hydrolysis and synthesis respectively at an acylase concentration of 1 mg ml^{-1}. The kinetic parameters are linked by the Haldane relation

$$K_{eq} = \frac{K'_M K_i V_{hydr}}{K_M V_{synth}} ,$$

where $K_{eq} = 3.6 \pm 0.4$ is the equilibrium constant of the hydrolytic-synthetic reaction of acetyl-L-methionine. The empirical Eqn.(3) [179] for the description of the action of a membrane reactor with acylase I under conditions where the reaction equilibrium begins to have an effect in essence confirms the kinetic mechanism (2):

$$v = \frac{V_{max}}{1 + (S_L + S_{0D})/K_1} \cdot \frac{S_L - (S_{0L} - S_L)^2/K_{eq}}{K_M [1 + (S_{0L} - S_L)/K_2] + S_L} , \quad (3)$$

where the S_L and S_D are the concentrations of acetyl-L-methionine and acetyl-D-methionine respectively (the symbols with subscript 0 represent the initial concentrations), $K_1 = 1.45 \pm 0.08$ M and $K_2 = (3 \pm 1) \times 10^{-3}$ M are the inhibition constants, $V_{max} = 3.37 \times 10^{-5}$ mol litre^{-1} s^{-1} is the maximum velocity at an acylase (I) concentration of 1 mg ml^{-1}, K_M $(0.8 \pm 0.5) \times 10^{-3}$ M is the Michaelis constant, and $K_{eq} = 2.75$ is the equilibrium constant.

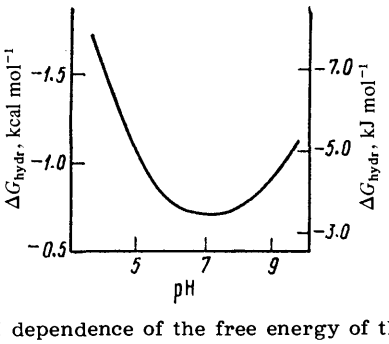


Figure 2. pH dependence of the free energy of the hydrolysis of acetyl-L-methionine.

Since the equilibrium constants of the hydrolytic-synthetic reactions of *N*-acetylaminoacids depend little on the nature of the aminoacid (Table 3), the proposed kinetic-thermodynamic approach is suitable for the description of the interaction of acylases with substrates having different structures.

There is no doubt that the experimental equilibrium constants of the hydrolytic-synthetic reactions of *N*-acetyl derivatives of aminoacids are not thermodynamic constants in the strict sense of the word, because the concentrations of the reactants in the reaction mixture are much higher than in dilute solutions for which the activity coefficient is unity. The lack of literature data for the activity coefficients of compounds of this kind, due to the exceptional difficulty and ambiguity of the measurements of these quantities, resulted in a general employment at the present time of equilibrium constants calculated from the concentrations of the reactants as estimates of the true thermodynamic equilibrium constants[56,57,78,82]. Since the equilibrium constant K_0 calculated in terms of the unionised forms of the reactants is independent of the pH and the entire contribution to the pH dependence of K_{eq} is due to the ionisation of specific ionogenic groups, it follows that, taking into account all the equilibria in system (4), it is possible to calculate the dependence of K_{eq} and hence of ΔG_{hydr} on the pH (Fig.2).[170,178]

Fig.2 shows that the equilibrium in this reaction is displaced towards synthesis precisely at the pH values where the majority of both the native acylases of animal and microbial origin and the immobilised preparations of these enzymes are active. This conclusion has a definite practical importance because the reversibility of the reaction in the stereoselective hydrolysis of the racemic acetylaminoacid reduces the productivity of the process:

$$\begin{array}{l} CH_3{-}CO{-}NH{-}CHR{-}COOH \overset{K_3}{\rightleftharpoons} CH_3{-}CO{-}NH{-}CHR{-}COO^- , \\ \quad \downarrow\uparrow K_0 \\ CH_3{-}COOH \overset{K_4}{\rightleftharpoons} CH_3{-}COO^- , \\ \quad + \\ NH_2{-}CHR{-}COOH \rightleftharpoons NH_2{-}CHR{-}COO^- , \\ \quad \downarrow\uparrow K_5 \qquad\qquad \downarrow\uparrow K_6 \\ NH_3^+{-}CHR{-}COOH \overset{K_1}{\rightleftharpoons} NH_3^+{-}CHR{-}COO^- ; \\ \Delta G = -RT \ln K_{eq} ; \\ K_{eq} = K_0 \dfrac{(1 + K_4/[H^+])(1 + K_1/K_2 + K_1/[H^+] + [H^+]/K_5)}{1 + K_3/[H^+]} ; \quad (4) \\ pK_1\ 2.3;\ pK_2\ 9.2;\ pK_3\ 3.8;\ pK_4\ 4.75;\ pK_5\ 7.4 . \end{array}$$

The search for new microbial acylases or the creation of immobilised enzyme preparations with a pH optimum of their catalytic activity in the pH range where the reversibility of the hydrolytic reaction does not have an effect even at high acetate ion concentrations would make it possible to eliminate this kind of deficiency. A possible method for the creation of immobilised acylase preparations with a modified pH optimum of their activity involves their incorporation in the structure of polyelectrolyte complexes.[180]

It is also of interest to note that the free energy of the hydrolysis of acetyl-L-methionine, calculated relative to the unionised forms of the starting materials and reaction products, is 7.46 kcal mol^{-1} (31.0 kJ mol^{-1}), i.e. the synthesis is a thermodynamically favourable process. The virtual failure to observe the synthesis of the acetamide linkage under the usual conditions is due to the fact that both the starting materials and the reaction products are present in the reaction mixture in the form of ions and the concentration of the unionised forms is negligible. The ΔG_0 obtained for acetyl-L-methionine exceeds somewhat the free energy of hydrolysis calculated relative to the unionised forms, usually obtained for the peptide bond[82], and shows that the synthesis of the acetamide linkage is thermodynamically even more favourable than the synthesis of the peptide linkage. Analogous results have been obtained also in the study of the reversible hydrolysis of *N*-phenylacetyl derivatives of aminoacids catalysed by penicillin amidase from *E. coli*[181,182].

The pig kidney acylase I exhibits a high stereospecificity. Among the large number of acetylaminoacids, only the D-isomer of acetylmethionine is appreciably hydrolysed by this enzyme; the ratio of the rates of hydrolysis of acetyl-L-methionine and acetyl-D-methionine, taken separately, is 10 000 : 1.[52] In the presence of L-methionine, the action of acylase I and acetyl-D-methionine is appreciably inhibited

and in the hydrolysis of the racemic acetyl-DL-methionine the ratio of the rates of hydrolysis of the L- and D-isomers is close to 40 000 : 1. A similar if not slightly greater ratio of the rates of hydrolysis of the optical isomers obtains for the acyl derivatives of other aminoacids. However, it has been observed that, when the acyl group is trifluoroacetyl, then a marked decrease of the stereospecificity of acylase I is observed for certain aminoacids[183].

The high stereospecificity of acylase I in the hydrolysis of acetyl and chloroacetyl derivatives of various aminoacids made it possible to resolve the racemates of many natural and synthetic aminoacids into optical isomers. On the other hand, it is necessary to note that acylase I is unsuitable for the resolution of the racemates of aspartic acid, proline, hydroxyproline, and aromatic aminoacids.

3. Microbial and Plant Acylases

Acylase activity (mainly in the hydrolysis of acetylmethionine) has been detected in tobacco leaves[184], in potato tubers, in many fruits (it is particularly high per unity weight in the radish and the pumpkin), in virtually all gramineous and leguminous plants (with the exception of polished rice whose treatment may lead to the breakdown of the enzyme system), and in the peel of mandarins, oranges, and figs[185,186]. An appreciable activity has been observed in the seeds of all the plants investigated and has been found to increase in the course of their growth[186,187].

Among all the plant acylases, only three enzymes have been partly purified and investigated: from rape seeds[188], from tobacco leaves[184], and from the seeds of palo verde (*Parkinsona Aculeata L.*).[189]

The enzyme from rape seeds hydrolyses enantioselectively the acetyl derivatives of aromatic and aliphatic aminoacids and methionine, the D-form not only not undergoing enzyme cleavage but also showing no influence on the hydrolysis of the L-form. The acetyl derivatives of glycine, glutamic acid, and proline as well as the benzoyl and benzyloxycarbonyl derivatives of aminoacids are resistant to the action of the enzyme. The pH optimum of the catalytic activity is in the range 7.2–8.8. Cobalt(II) ions activate the acylase approximately by a factor of 50, but those of calcium(II), iron(II), magnesium(II), nickel(II), and zinc(II) are 10 times less effective. The enzyme activity is inhibited by *p*-chloromercuribenzoate (PCMB), but *o*-phenanthroline , 8-hydroxyquinoline, or *N*-ethylmaleimide do not influence the catalytic activity[188].

An enzyme with a much narrower substrate specificity, which hydrolyses only *N*-acetyl-L-arginine, *N*-acetyl-L-cysteine, *N*-acetyl-DL-methionine, and, significantly less effectively, *N*-formyl-DL-methionine, has been partially purified from tobacco leaves. The pH optimum of its catalytic activity is displaced to the alkaline region compared with the pig kidney acylase I and depends on the nature of the substrate hydrolysed. Cobalt(II) ions activate the tobacco leaf acylase, the degree of activation increasing during purification. PCMB fully inhibits the enzyme activity at a concentration of 0.5 mM, but iodoacetate (1.5 mM) and EDTA (20 mM) do not influence the catalytic properties of tobacco leaf acylase[184].

The acylase activity in the palo verde seeds is concentrated mainly in the embryo and in the cotyledons. The acylase has been purified by a factor of 75 and its properties have been found to resemble closely those of the acylase isolated from rape seeds[189]. The acylase from the palo verde seeds effectively cleaves a wide set of acetyl and formyl derivatives of aromatic and aliphatic aminoacids, *N*-formyl-L-methionine being the best substrate. The acyl derivatives of D-aminoacids are hydrolysed to only a very slight extent. The pH optimum of the catalytic activity depends on the nature of the substrate hydrolysed and is located in the range 7.0–9.0. Cobalt(II) ions activate the enzyme approximately by a factor of 1.5 and greatly increase its stability during isolation. On the other hand, it has been noted that the acylase retains its activity after dialysis and electrophoresis, i.e. it is most probably not a metalloenzyme, because the metal ion is bound very firmly to the protein globule. The acylase from the palo verde seeds is inhibited by SH reagents like the other acylases considered[189].

The properties of the acylases under examination are close to those of the pig kidney acylase I. Like acylase I they exhibit a high stereospecificity (methionine derivatives are hydrolysed most effectively), are activated by cobalt(II) ions, and are sensitive to the action of SH reagents. A characteristic difference between plant acylases and acylase I is the displacement to the alkaline region of the pH optimum of the catalytic activity and the fact that the plant acylases are capable of hydrolysing the derivatives of not only aliphatic but also aromatic aminoacids. Such broad substrate specificity makes possible the employment of plant acylases for the resolution of aminoacid racemates. However, one should note that even greater prospects, which have already been embodied in practice, are associated with the acylases isolated for various micro-organisms (see Table 4).

4. ε-*N*-Acyl-L-lysine Amidohydrolase

Their exists an enzyme capable of hydrolysing only the L-isomer when it acts on racemic ε-*N*-acyl-DL-lysine (ε-*N*-acyl-L-lysine amidohydrolase, EC 3.5.1.17). It is of interest to note that in this case ε-lysine acylase exhibits stereospecificity in the hydrolysis of a bond which is comparatively remote from the asymmetric centre in the substrate molecule. The ε-lysine acylase activity was first detected in the KT 83 soil bacteria[190]. Later the ε-lysine acylase activity was found in a number of micro-organisms: moulds (particularly *Aspergillus*), the *Rhodotorula glutinis* yeast[191], and the *Achromobacter* and *Pseudomonas* bacteria (particularly *Achromobacter pestifer*[192]). The optimum conditions for the growing of *A. pestifer* as a producer of ε-lysine acylase activity have been elucidated[193] and the enzyme itself has been purified as far as the electrophoretically homogeneous state[194]. The enzyme hydrolyses all possible ε-acyl derivatives of lysine: acetyl, chloroacetyl, di- and tri-chloroacetyl, iodoacetyl, n-butyryl, caproyl, caprylyl, glycyl, benzoyl, phenylacetyl, benzyloxycarbonyl, *p*- and *m*-nitrobenzoyl, and naphthoyl derivatives, but neither α-acyl- nor diacyl-L-lysine undergoes enzymic hydrolysis. The replacement of a hydrogen atom by an alkyl group in the ε-NH_2 group also renders the substrate non-hydrolysable[195]. The Michaelis constants for the hydrolysis of the ε-chloroacetyl, ε-acetyl, and ε-benzoyl derivatives of L-lysine are respectively 0.29×10^{-3}, 0.5×10^{-3}, and less than 0.1×10^{-3} M.[196] The enzyme is inhibited by silver(I), mercury(I), and mercury(II) ions, PCMB, chloroacetone, and iodoacetate. The inhibition by PCMB is fully removed by the addition of cysteine. EDTA has little effect, while iron(III) and aluminium(III) ions (at a concentration of 1 mM) and nickel(II), cobalt(II), manganese(II), calcium(II), strontium(II), and cadmium(II) ions (at a concentration 10 mM) activate ε-lysine acylase to the extent of 20–30%. The pH optimum of the activity of the enzyme from *A. pestifier* is 4.8–5.2, which differs from that of the ε-lysine acylases from *Pseudomonas* and *Aspergillus oryzae*, for which the pH optima are respectively 6.0 and 8.2–8.4.[197]

An enzyme which hydrolyses stereoselectively the *N*-δ-acyl derivatives of ornithine, has been detected in the cells of the *Pseudomonas* KT 80 strain[198], but it has been scarcely investigated.

Table 4. The acylase activities of various micro-organisms.

Micro-organisms	Substrate specificity		Enzyme inhibitors and activators	pH optimum of activity	Refs.
	hydrolyses	does not hydrolyse			
Str. caespitosus	Ac-L-aminoacids	D-isomers	NI : bivalent cations, EPTA	7.0—8.0	[199]
Bact. cadaveris	Form-Gly, -Tyr Ac-Tyr	Ac-, Clac-Asp		7.0—8.0	[200]
Micrococcus n. sp.	ditto	ditto	—	7.0—8.0	[200]
Hydrocarbon oxidising micro-organisms	Ac-Leu, -norLeu, -Val, -Met, Bz-Leu	Ac-Trp, Bz-Asp	—	—	[201]
Bacillus brevis *Bacillus subtilis* *Bacillus megaterium* Micrococcus lysodeckticus	Ac-*L*-Met	Ac-*D*-Met	—	—	[202]
Corynebacterium glutamicum	Ac-*L*-Glu	Ac-*D*-Glu	—	—	[203]
E. coli B	Form-L-Met, Ac-L-Met, Ac-L-aminoacid		A : Co(II)(5×10^{-5}M), Ni(II)(10^{-5}M), Fe(II)(10^{-2}M), Mn(II)(10^{-2}M); I : Zn(II), EDTA	6.5—6.6	[204]
E. coli 160-37	Form-L-aminoacids		EA : Mn(II)(10^{-3}M), Co(II) (10^{-4}M)	7.2	[204]
E. coli ATCC 9637	Ac-Met, -Orn	Ac-Ala, -Leu, -Val, -Glu, Clac-Tyr, Bz-Arg	A : Co(II); I : Cu(II), Zn(II), Ni(II), EDTA	7.0	[205]
E. coli	Phac-*L*-Ala, -*L*-Val, -*L*-Ambut, -*L*-Leu, -*L*-Phe	D-isomers	—	—	[206, 207]
Ditto	Ac-*L*-Ala, -*L*-Met, Clac-*L*-Ala, -*L*-Met, -*L*-Asp, -*L*-Leu, -*L*-Phe	D-isomers Clac-L-Tyr, -L-Trp	A : Co(II)	—	[208]
Neursopora crassa	Phac-L-aminoacids				[209]
Mycobacterium smegmatis	Palmityl-L-Asp, -L-Val, L-Phe, decanoyl-L-Asp, lauryl-L-Asp	Ac-, butyryl-, hexanoyl-, octanoyl-L-Asp	A : alkali metal ions; I : Cu(II), Hg(II)	5.7—7.3	[210, 211]
Ditto	Ac-*L*-Val, -*L*-Asp, Clac-*L*-Phe		A : bivalent cations; I : Cu(II), Hg(II)	—	[210, 211]
Mycobacterium avium	palmityl-L-Asp, -L-Val, -L-Phe		NI : Cu(II), Hg(II)	6.2	[212]
Ditto	Ac-*L*-Val, *L*-Asp, Clac-*L*-Phe	—	I : Cu(II), Hg(II)	7.4	[212]
Mycobacterium phei	lauryl-L-Phe, -L-Ala, -L-Ambut, -L-Met, -L-Glu, Bz-L-Ala, -L-Ambut	—	—	—	[213]
Staphylococcus oureus	Bz-Gly, -Phe	—	—	—	[213]
Brewer's yeast	Ac-*L*-Met, Clac-*L*-Ala, -*L*-Leu, -*L*-Phe, -*L*-Trp, Gly-*L*-Met	—	—	—	[214]
Pseudomonas ATCC 11299B	Form-Asp, Clac-Asp	Ac-Met, Form-Leu	EA : Co(II); A : Fe(II)	7.0	[215]
Ditto	Form-, Ac-, Clac-Asp	Ac-Met, Form-Leu	EA : Co(II); A : Fe(II)	8.0	[215]
Soil pseudomonads	Ac-L-Asp, -L-Asn, Bz-L-Asp, dipeptides with L-Asp or L-Asn at the C-end	D-isomers, Ac-, Bz-aminoacids	Ea : Co(II), Zn(II)	—	[216, 217]
Ditto	Ac-*L*-Ala, Bz-*L*-Ala	ditto	Ditto	—	[218]
»	Ac-L-Glu, -L-Gln, Bz-L-Glu, -L-Gln, dipeptides with L-Glu or O-Gln at C-end	—	—	—	[219]
Pseudomonas KT83	Bz-D-Phe, -D-Phg, -D-*p*-nitro-Phe, -D-β-phenylSer, aromatic diClac-D-aminoacids	L-isomers	—	—	[220, 221]
Pseudomonas KT 84	diBz-*L*-Lys **, Bz-*L*-Ser, -*L*-Thr, -*L*-Orn, -*L*-Met, -*L*-Glu, -*L*-Asp, -*L*-Leu, -*L*-Val	D-isomers	—	—	[222, 223]
Pseudomonas KT 85	Bz-*L*-β-phenylSer, -*L*-isoLeu	D-isomers	—	—	[224, 225]
Pseudomonas KT 104	Ac-*L*-Trp	Ac-*D*-Trp	—	—	[226]
Pseudomonas KT 202, KT 205	Bz-*L*-Thr, diBz-*L*-Lys **, Ac-*L*-Trp, -*L*-Met	D-isomers			[227]
Pseudomonas KT 218	Bz-, Ac-L-aminoacids with straight C_6, C_8, C_{12}, or C_{14} chain; Bz-L-Thr	D-isomers	—	—	[228]
Pseudomonas KT 224	Ac-*L*-Met	Ac-*D*-Met	—	—	[229]
Pseudomonas KT 230, KT 231, KT 232, KT 233	diBz-L-Lys**; Bz-L-Phe, -L-Thr, -L-aminoacids (aliphatic)	D-isomers	—	—	[230, 235]
Pseudomonas KT 251, KT 256	Ac-*L*-Trp	Ac-*D*-Trp	—	—	[235]
Pseudomoans KT 301	diBz-*L*-Lys **	diBz-*D*-Lys	—	—	[236]
Pseudomonas KT 303 KT 305	Bz-*L*-Trp	Bz-*D*-Trp	—	—	[233]
Pseudomonas KT 313	diBz-*L*-Lys **, α-Phac-ε-Bz-*L*-Lys	D-isomers	—	8.0	[237]
Pseudomonas KT 801	Bz-, Phac-, diClac-octanoyl-L-aminoacids*	D-isomers	A : Mg(II)*; I : Co(II), Cu(II), Mn(II), *o*-phenanthroline		[238]
Pseudomonas AAA 6020	Phac-L-Val, -L-Leu, -L-Glu, -L-Ala, -L-Met, -D-aminoacids	Ac-, Bz-aminoacids	I : Hg(II)*, Zn(II)*, Co(II) (10^{-3}M)*	8.0	[239]
Pseudomonas AAA6029	Bz-, Ac-D-Phe-, -D-Met, -D-Leu, -D-Ala, -D-Val	Phac-D- and -L-aminoacids, Bz-, Ac-L-Phe, -L-Met, -L-Leu, -L-Ala, -L-Val, Ac-D-L-amino-acids	A : L-Cys(3×10^{-3}M); I : Hg(II), Zn(II)(10^{-3}M), PCMB(10^{-3}M); NI ; Ca(II), Co(II), Mg(II) (10^{-3}M)	10.5 (Bz-*D*-Phe) 6.8 (Ac-*D*-Phe)	[240]
Micrococcus agilis	Ac-Phe-, -Met, -Val, -Leu, Clac-Phg, -Tyr, -Glu	Ac-Asp, Ac-*D*-Phe	I : Ag(I)*, Mn(II), Pb(II), Cu(II), Cd(II), Hg(II)(10^{-3}M), iodo-acetamide, PCMB, *o*-phenanth-roline, mercaptoethanol	7.0	[241]
Streptomyces tuirus IFO 13418	Ac-*D*-Phg, -*D*-Leu, -*D*-Ala, -*D*-Met, -*D*-Val, -*D*-Phe, -*D*-Tyr, -*D*-Trp, -L-Met	L-isomers	I : Ag(I), Hg(II)(10^{-5}M); NI : NaN_3, NaCN	7.5	[242]
Pseudomonas aeruginosa	Ac-L-Glu, Form-L-Glu, fluoroacetyl-L-Glu, propionyl-L-Gly, Ac-L-Gln, -L-Met, -L-Ala, -Gly	butyryl-L-Glu, Form-L-Met*, Ac-L-Ser*, -L-Asn*, -L-His*, -L-Asp*,	EA : Co(II), Zn(II), Mn(II), Mg(II) (10^{-3}M); I : PCMB (10^{-5}M); NI : *N*-ethylmaleimide	6.5	[243]
Penicillium vinaceous	aromatic Ac, Clac-L-amino-acids	D-isomers	A : Co(II)(10^{-3}M) I : Hg(II), Mn(II)	5.6—5.8 (Ac-amino-acids)	[244—247]
Penicillium oxalicum	diAc-*L*-Lys, Ac-*L*-Met, -*L*-Ala, -*L*-Glu, *L*-Leu *, -*L*-Val *, -*L*-isoLeu *, -*L*-His *, -*L*-Asp *, Clac-*L*-Ser, -*L*-Val *	—	—	7.6-7.8 (Clac-amino-acids)	
Aspergillus oryzae	ε-Bz-α-Ac-L-Lys**, Clac, Ac-aminoacids	D-isomers	A: Co(II), Zn(II) *, Cd(II) *, Mn(II) *, Cu(II) * (10^{-3} *M*)	7.5	[248—251]

Table 4 (cont'd).

Micro-organisms	Substrate specificity: hydrolyses	Substrate specificity: does not hydrolyse	Enzyme inhibitors and activators	pH optimum of activity	Refs.
Aspergillus avamori 78-2 *Streptoverticillium*	Ac-Trp, -Met Ac-*L*-Met, -*L*-Leu, -*L*-Phe, -*L*-Trp, -*L*-Phg	D-isomers	— —	7,0	[252] [253]

Notation: A = activators, I = inhibitors, NI = no influence on activity, EA = essential for activity, Form = formyl, Clac = chloroacetyl, norLeu = norleucine, Ambut = α-aminobutyric acid, Phg = α-aminophenylacetic acid (phenylglycine), and isoLeu = isoleucine.

*Weakly hydrolyses or activates.

**The hydrolysis of the diacyl derivatives of lysine takes place only at the α-amino-group (the hydrolysis of the ε-amino-group was examined in Section VI).

Table 5. The preparation and properties of immobilised acylases.

Methods of immobilisation, enzyme	Retention of activity, %	Change in properties of immobilised enzyme relative to native enzyme	Refs.
Pig kidney acylase I			
Adsorption on A-50 DEAE-sephadex	—	IT	[262]
on silica gel or C-80 silochrome	50	shift of pH optimum by 1 to alkaline region	[263,264]
on silica gel coated by a layer of lecithin, cholesterol, or inosine	25—45	ditto	[264]
on DEAE-cellulose	—	—	[264]
on ceramic carriers based on Al_2O_3, SiO_2, and TiO_2	H	pH optimum becomes very broad (7.5-9.5)	[265]
on silochrome coated with a protein or a synthetic polymer	15	—	[266,267]
Bonding to "Enzacryl-AA"	30	shift of pH optimum to alkaline region by 0.4; IT	[268]
to silochrome by means of γ-aminopropyltriethoxysilane and glutaraldehyde	H	—	[269]
to DEAE-cellulose via triazine dyes	H	—	[269]
to silochrome via diazotised *m*-phenylenediamine	H	—	[269]
to insoluble polyamide (copolymer of acrylamide, methyl acrylate, and *N,N'*-methylenebisacrylamide) via an amide linkage	50—100	IT	[270]
to COOH-containing gels via soluble carbodi-imides	—	—	[271]
to water-soluble dialdehyde-epidex and dialdehyde-dextran	L	—	[272]
Incorporation in polyacrylamide gel by oxidative-reductive polymerisation or photopolymerisation	6—12	—	[266]
Incorporation in polyacrylamide gel by radiopolymerisation	25—45	change in substrate specificity	[273]
Acylase from *Aspergillus ochracens*			
Covalent bonding to cell mycelia with the aid of albumin and glutaraldehyde	80	Increase of resistance to action of inhibitors; IT	[274]
Acylase from *Aspergillus oryzae*			
Adsorption on activated charcoal, acid, neutral, and alkaline alumina, and silica gel	<1		[275]
on tannin bonded to aminohexylcellulose	20—25		[276]
on PAB-cellulose	0	shift of pH optimum to acid region by 0.5-1; IT	[275,277, 278]
on TEAE-cellulose	51.5		
on DEAE-cellulose	55.2		
on C-50 KM-sephadex	0	shift of pH optimum to acid region by 0.5-1; IT	
on A-25 and A-50 DEAE-sephadex	56—59		
on IRC-50, IR-4B, and RI-45 amberlites	0		
Covalent bonding to diazotised PAB-cellulose	5.3		[279,280, 281,282]
to diazotised arylamino-glass	43.5		
to diazotised "Enzacryl-AA"	3.6		
to CM-cellulose azide	0		
to BrCN-activated cellulose	1.0		
to BrCN-activated sephadex	1.2		
to chloroacetycellulose	11.3	shift of pH optimum to alkaline region by 0.5-1; IT	
to bromoacetylcellulose	28 0		
to iodoacetylcellulose	39.0		
to arylamino-glass	20—40	shift of pH optimum to acid region by 0.5; IT	
Cross-linking on carrier (AE-cellulose) by a bifunctional reagent			[283]
1,4-dibromobutene	0.4		
1,4-dichlorobutene	0.4		
dicyclohexylcarbodi-imide	1.2		
di-iodomethane	0.3	—	
glutaraldehyde	0.6		
hexamethylene di-isocyanate	1.6		
tolylene di-isocyanate	0.2		
Cross-linking by a bifunctional reagent			[283]
glutaraldehyde	14.7	—	
tolylene di-isocyanate	1.3		
Incorporation in polyacrylamide gel	52.8	shift of pH optimum to acid region by 0.5; IT	[284]
Incorporation in carrageenan gel	50	IT	[285]
Microencapsulation			
in nylon	36.0	—	[284]
in polycarbamide	15.0		
in ethylcellulose	10.4		

Table 5 (cont'd).

Notation. H = high, L = low, and IT = increase of thermal stability.

5. Industrial Utilisation of Microbial Acylases

Utilisation of microbial acylases for the resolution of amino-acid racemates into optical isomers constitutes at present the only method which has found an industrial application. For this reason there is an unusually great interest in micro-organisms capable of hydrolysing *N*-acylated aminoacids. The available literature data on microbial acylases are compiled in Table 4.[199-253]

It is seen from the data in Table 4 that microbial acylases exhibit a virtually no substrate specificity and hydrolyse all possible acyl derivatives of all the natural aminoacids except proline, hydroxyproline, and a number of synthetic α-amino-acids. It is of interest to note that the majority of acylases exhibit a pronounced stereospecificity and hydrolyse selectively only the acyl derivatives of the L-isomers of amino-acids, but, among the mutants of soil micro-organisms, it has been possible to detect an enzyme which catalyses the hydrolysis of acylated D-aminoacids with a fairly broad substrate specificity[220,221,240]. The presence of acylases stereospecific

to both L- and D-isomers gives rise to the hope that it will be possible to select a scheme for the aminoacid racemate resolution process depending on which of the two optical isomers has to be obtained.

However, despite the very large number of studies devoted to the conditions under which the enzyme producers are cultivated, the isolation and partial purification of acylases, the development of methods for the preparative resolution of racemates with the aid of the preparations obtained, the immobilisation of acylases from micro-organisms (the immobilisation of acylases will be considered in detail below), and the action of reactors based on an immobilised enzyme, hitherto neither the acylase from *Aspergillus oryzae* nor the acylase from soil micro-organisms have been obtained in a sufficiently pure form; nothing is also known about the mechanism of the action of these enzymes. Undoubtedly the knowledge of the mechanism of the enzyme action would assist in the search for optimum process conditions and in the selection of the type of catalyst for the industrial resolution of racemates using acylases from micro-organisms.

A whole series of methods for the resolution of aminoacid racemates into optical isomers with the aid of soluble acylases of microbial origin have now been patented[254-261], but there is no doubt that the future in this field belongs to immobilised enzymes or cells.

The extensive technological possibilities for the application of immobilised biocatalysts, in particular aminoacid acylases, have led to numerous studies on the immobilisation of the pig kidney acylase I and particularly the acylases from micro-organisms. The available literature data on the methods of preparation and properties of immobilised aminoacid acylases are compiled in Table 5.[262-285] The table shows that a high retention of the activity of the microbial acylase on immobilisation is achieved in the following methods: adsorption on DEAE- and TEAE-cellulose or DEAE-sephadex, covalent bonding to diazotised arylamino-glass or halogenocellulose, bonding via glutaraldehyde to arylamino-glass, incorporation in a polyacrylamide gel, and microencapsulation using nylon. However, the simplicity of preparation, low-cost, high operational stability, and the possibility of regeneration by the adsorption on the carrier of a fresh portion of enzyme corresponding to the loss of activity[286] (Fig.3) make acylase sorbed on DEAE-sephadex the most suitable biocatalyst for the practical resolution of racemates[287]. An industrial apparatus for the resolution of alanine, methionine, phenylalanine, valine, and tryptophan has been devised on the basis of this biocatalyst (Fig.4).[288] A 0.2 M solution of acetyl-DL-methionine, containing 5×10^{-4} M cobalt(II), is passed through a 1000 litre column containing the acylase from *Aspergillus oryzae* immobilised on DEAE-sephadex at a rate of 2000 litre h^{-1} at 50 °C and pH 7.0. The free L-methionine is precipitated when the eluate is evaporated. The yield is 91% and $[\alpha]_D^{25} = +23.4°$ after recrystallisation from water. The acetyl-D-methionine in the mother liquor is heated at 60 °C with acetic anhydride for racemisation and acetyl-DL-methionine is isolated and reused as the substrate[287].

Fig.5 presents a comparison of the usual method with a soluble acylase and the continuous process based on the immobilised enzyme. Firstly, there is a sharp reduction of the consumption of the biocatalyst and, secondly, there is an appreciable decrease of the amount of labour required and the purification procedure is simplified, which makes it possible to obtain a larger amount of the final product from the same amount of the starting materials. All these factors taken together make it possible to decrease by a factor of 2 the cost of the manufacture of L-aminoacids when an immobilised acylase is used.

The examples presented show that the enzymic conversion of racemates into optically pure aminoacids is already a method which has found technological applications, together with other procedures, for the preparation of these compounds. It is noteworthy that there is at present no universal method for the manufacture of the entire set of essential aminoacids. In each specific instance the procedure for the manufacture of a particular aminoacid must therefore be determined individually as a function of the raw materials, the amount required, the required purity, the availability of the necessary biocatalysts, and many other factors. However, there is no doubt that biotechnological processes employing enzymes capable of achieving the enantioselective conversion of the simplest aminoacid derivatives will find, in combination with the chemical synthesis of the starting materials, still more extensive applications in the immediate future.

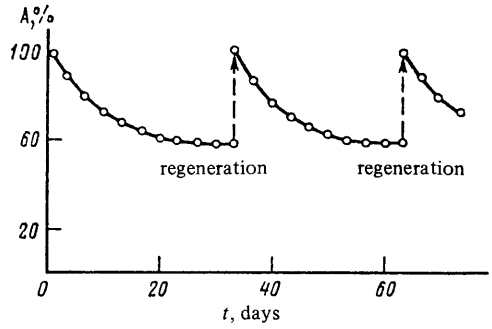


Figure 3. The stability and regeration of a column containing the acylase from *Aspergillus oryzae* immobilised on DEAE-sephapez; A = activity.

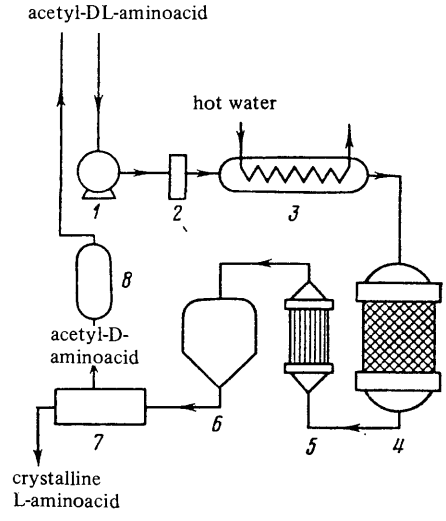


Figure 4. Industrial apparatus for the resolution of aminoacid racemates based on the acylase from *Aspergillus oryzae* immobilised on DEAE-sephadex[283]; 1) pump; 2) filter; 3) heat exchanger; 4) reactor; 5) evaporator; 6) crystalliser; 7) separator; 8) racemiser.

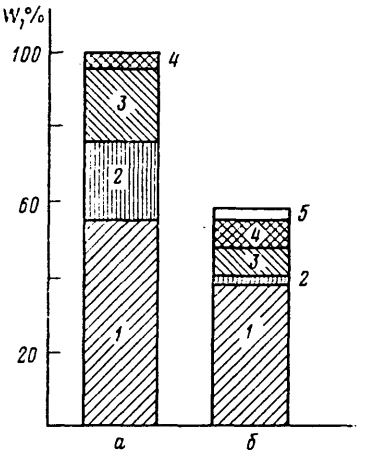


Figure 5. The relative costs W in the industrial resolution of aminoacid racemates with the aid of the acylase from *Aspergillus oryzae*, both soluble and immobilised on DEAE-sephadex: *a*) periodic process (soluble enzyme); *b*) continuous process (immobilised enzyme)[283]; costs of different process components: 1) substate; 2) enzyme; 3) labour; 4) fuel; 5) carrier for immobilisation.

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The Debenzhydrylation and Transbenzhydrylation Reactions

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The review describes various reactions involving the cleavage of benzhydrylated compounds and their rearrangements and also the use of the benzhydryl group as a protective group. The lability of the bonds between the benzhydryl group and oxygen, sulphur, nitrogen, carbon, and other atoms is demonstrated.
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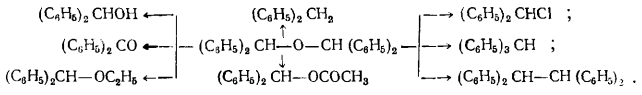
I. INTRODUCTION

There are reviews in the literature on the mobility of the benzyl (phenylmethyl) [1] and trityl (triphenylmethyl) [2] groups. The mobility of the benzhydryl (diphenylmethyl) group, which is of both theoretical and preparative interest, has also been known for a long time. However, until recently there have been no surveys in the literature of data on this problem. In the present review an attempt is made to fill this gap. A particularly large number of studies on the debenzhydrylation and transbenzhydrylation reactions have been published during the last two decades.

II. THE CLEAVAGE OF THE BONDS BETWEEN THE BENZHYDRYL GROUP AND OXYGEN, SULPHUR, AND NITROGEN ATOMS

1. The Bond between the Benzhydryl Group and an Oxygen Atom

As early as the end of the past century, Nef[3] showed that the reaction of dibenzhydryl ether with water gives rise to benzhydrol, the reaction with benzene produces triphenylmethane, the reaction with ethanol gives rise to benzhydryl ethyl ether, and the product of the reaction with acetic acid is benzhydryl acetate. When dibenzhydryl ether reacts with hydrogen chloride, it is converted into chlorodiphenylmethane[4], its reaction with nitrogen dioxide converts it into benzophenone[5], it can be hydrogenated to diphenylmethane[6], and on treatment with potassium butoxide it is converted into 1,1,2,2-tetraphenylethane[7]:

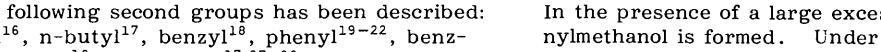


The reversibility of the reaction of chlorodiphenylmethane and its derivatives with ethanol has been demonstrated in a number of studies[4,8-11]. The decomposition of benzhydryl ethers with the following second groups has been described: ethyl[12-15], allyl[16], n-butyl[17], benzyl[18], phenyl[19-22], benzhydryl[7,12,23-26], trityl[18], and others[17,27-29]. The benzhydryl ethers of benzoin[30], hydroquinone[31], and cellulose[32], α-bromo-,[14] 4,4′-dinitro-,[7] and 4,4′-dimethoxy-benzhydryl ethers[15], dixanthydryl ether[33], *O*-benzhydryloximes[34], *O*-benzhydryl-α-aminoperoxides[35], as well as benzophenone ketals[12,36-46] have been decomposed.

Benzhydryl ethers are readily decomposed by liquid potassium–sodium alloy even at room temperature[12]. Shorygin showed[19] that, on treatment with sodium, benzhydryl phenyl ether decomposes with formation of diphenylmethane, *sym*-tetraphenylethane, phenol, and triphenylmethanol. In his survey of extensive researches into the decomposition of ethers by metallic sodium, Shorygin concludes that the cleavage of all the ethers proceeds via one pathway—the oxygen atom always remains bound to the phenyl or tolyl residue, since the benzhydryl, trityl, and naphthylmethyl groups are comparatively weakly bound to oxygen.

On reaction with hydrogen bromide in acetic acid, benzhydryl ethyl ether is converted to bromodiphenylmethane[5]. On direct chlorination of allyl benzhydryl ether, the addition of chlorine atoms to the double bond of the olefin is also accompanied by the dissociation of the bond between the benzhydryl group and the oxygen atom with formation of chlorodiphenylmethane[16]. Catalytic hydrogenation of benzhydryl benzyl ether in the presence of Raney nickel gives rise to diphenylmethane and benzyl alcohol, while hydrogenation of benzhydryl trityl ether produces triphenylmethane and diphenylmethanol, which is converted into diphenylmethane[18]. In the former case the cleavage takes place at the $O-CH(C_6H_5)_2$ bond, while in the latter case dissociation of the $O-C(C_6H_5)_3$ bond has been postulated. Certain benzhydryl ethers undergo thermal decomposition[15,22,32].

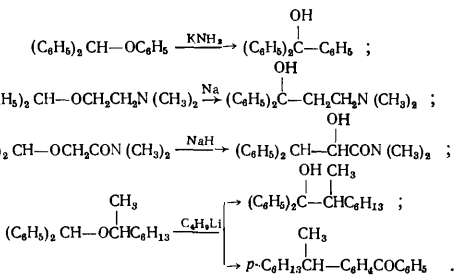
O-Benzhydrylhydroxylamine and its derivatives undergo interesting reactions[47-51]. Their oxidation by lead tetraacetate gives rise to a mixture of substances, including the products of the migration of the benzhydryl group from the oxygen to the nitrogen atom. Treatment of *O*-benzhydryl-*N*-tosylhydroxylamine with sodium hydride or butyl-lithium leads to the formation of the corresponding salts whose pyrolysis gives rise to benzophenone oxime in 100% yield as a result of the loss of the sulphinate group and the migration of the benzhydryl group from the oxygen to the nitrogen atom:



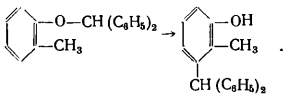
In the presence of a large excess of sodium hydride, diphenylmethanol is formed. Under the same conditions, *O*-benzhydryl-*N*-methyl-*N*-tosylhydroxylamine gives rise to diphenylmethanol, benzophenone, and *N*-methyltoluene-*p*-sulphonamide.

In 1924 Shorygin[52,53] discovered the carbinol rearrangement. He showed that, on heating with sodium wire in a sealed tube, benzyl phenyl ether produces diphenylmethanol.

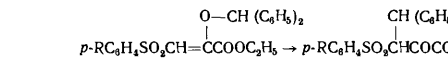
Subsequently Wittig and Lohmann[36,54] observed an analogous rearrangement of benzhydryl methyl ether, which isomerises to diphenylmethylmethanol on treatment with phenyl-lithium. A rearrangement occurring when the dimethylketal of benzophenone is treated with powdered sodium has been described by Schlenk and Bergmann[36] and was subsequently confirmed by Wittig ahd Happe[36] [Ref.20? (Ed.of Translation)]. An analogous rearrangement involving these and other benzhydryl ethers was achieved still later with the aid of metallic sodium[55], sodium hydride[56], potassium hydroxide[7,30], potassium amide[57], butyl-lithium[58], and lithium dimethylamide[59]. The reaction proceeds in accordance with the following scheme:



It has been found[60] that the benzhydryl ether of *o*-cresol undergoes a rearrangement with formation of 3-benzhydryl-2-methylphenol on heating for 5 h at 150 °C in the presence of zinc chloride:

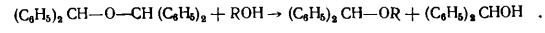


It has been observed quite recently[61] that the ethyl esters of β-arenesulphonyl-α-diphenylmethoxyacrylic acids rearrange quantitatively in the temperature range from 160° to 190 °C to the ethyl esters of β-arenesulphonyl-β-diphenylmethylpyruvic acids:



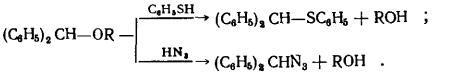
According to the authors, the *C*-alkylation products are apparently formed as a result of suprafacial [1,3]-sigmatropic rearrangement of the benzhydryl group.

The reactions of dibenzhydryl ether with butyl and benzyl alcohols proceed with displacement of one benzhydryl group[62]:



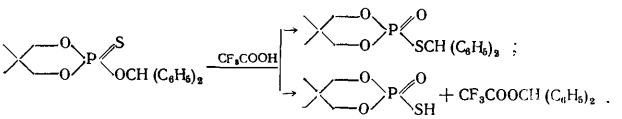
When butyl alcohol reacts with benzhydryl trityl ether, butyl trityl ether is formed together with benzhydryl butyl ether[62]. Yet another instance of the replacement of the benzhydryl group in ethers by the methyl group has been described recently[63]. The yields of the products of all these reactions are high.

It has been shown[28,64] that, on reaction with thiophenol and hydrazoic acid in the presence of trifluoroacetic acid, alkyl benzhydryl ethers are quantitatively converted into the corresponding sulphide and azide:



As early as 1865, Linnemann[65] pointed out the ready decomposition of the benzhydryl esters of acetic, benzoic, and succinic acids. According to Cheeseman's data[5], benzhydryl nitrate decomposes even at room temperature with formation of dibenzhydryl ether and benzophenone.

The hydrolysis of benzhydryl nitrate[5,66], benzhydryl formate[67,68], benzhydryl acetate[67-71], and benzhydryl benzoate[68,71], the ethanolysis of the last compound[72,73], the pyrolysis of the benzhydryl esters of nitric[5,74] and acetic[75,76] acids, the reduction of benzhydryl acetate[77] and benzhydryl benzoate[78], and the cleavage of other benzhydryl esters[79-85] have been described. Many studies have been devoted to the investigation of the kinetics and mechanisms of the above processes[66-73,81]. Thiocarbonates[86,87] and xanthates containing the benzhydryl group[88-90] have also been decomposed. The debenzhydrylation and transbenzhydrylation reactions of benzhydryl esters containing phosphorus[91-95], germanium[96], and silicon[96-100] atoms are of interest. For example[95]:



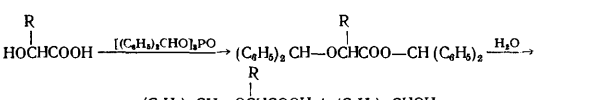
Chlorodiphenylmethane has been obtained in 90% yield by the reaction of benzhydryl acetate with acetyl chloride[77]. French workers[101,102] showed that, when benzhydryl acetate and benzoate are used in the Reformatskii reaction, the latter proceeds anomalously with formation of diphenylmethane and 1,1,2,2-tetraphenylethane.

Benzhydryl nitrate has been used successfully as the benzhydrylating agent for ammonia, hydrozine, amines, the amides of carboxylic and sulphonic acids, alcohols, mercaptans, urethanes, heterocyclic bases, and other compounds[5]. The kinetics of the benzhydrylation of aromatic hydrocarbons[103] and anisole[104,105] by benzhydryl acetate have been investigated:



Benzhydryl benzoate can be used for the benzhydrylation of thiophenol[64].

Methods for the synthesis of the benzhydryl esters of phosphoric acid and their employment for phosphorylation and the removal of protective groups have been investigated[106-109]. A new method of synthesis of benzhydryl esters based on the reactions of alcohols and carboxylic acids with tribenzhydryl phosphate was published in 1978.[110,111] In the reactions with hydroxyacids two benzhydryl groups are introduced one of which is removed more readily:



The benzhydryl protective group has found applications in the synthesis and the investigation of the properties and structures of nucleosides, nucleotides, and oligonucleotides[106,109,112,113]. In the study of the comparative stabilities under various conditions of the benzhydryl and trityl esters of uridine 3'-phosphate, it was shown that the trityl ester is more resistant to hydrolysis in 80% acetic acid and 50% formic acid than the benzhydryl ester[109].

The protection of the phenolic hydroxyl by the benzhydryl group has found applications in the synthesis of polyesters (including macrocyclic polyesters) containing two dinaphthyl residues[114,115]. The benzhydryl protective group has been used to obtain the esters of phenols and depsides[116-118]. Here one should mention also the protection of phenols and catechols by the diphenylmethylene group[118-126].

The benzhydryl group has found extensive applications for the protection of the carboxy-group in the synthesis and the investigation of the properties and structures of aliphatic

and aromatic carboxylic acids containing from several to several tens of carbon atoms[27,116-118,127-134]. Catalytic hydrogenation is most often employed for the removal of the protective group[27,116,118,127-131,133,134]. The catalyst employed is usually palladium. Furthermore, the benzhydryl protective group can be removed with the aid of trifluoroacetic[128,132] and 80% acetic[117] acids, a saturated solution of hydrogen chloride in acetic acid[132], hydrogen chloride or bromide in nitromethane[133], and basic reagents in ethanol and dioxane[132].

Khorlin and Privalova[135] were the first to describe the protection by the benzhydryl group of the carboxy-group in the most common representative of sialic acids—*N*-acetylneuraminic acid. This protective group and the methods for its removal have been investigated also for various reactions of other carbohydrate derivatives[80,128,131,136-138]. The selective hydrolysis of the protective group has been indicated[80].

The benzhydryl group has found extensive applications for the protection of the carboxy-group in the synthesis and investigation of β-lactam antibiotics, including nocardicin, penicillin, and particularly cephalosporin[134,139-216]. The benzhydryl protective group has been used also in the synthesis of other antibiotics[217] and analogues of the anti-inflammatory agent indomethacin[218] and derivatives of benzofuranone[219]. 4-Chloro-,[106] 2-nitro,[220] and 4-nitrobenzhydryl protective groups[221] have been described in the literature.

The instability of the benzhydryl esters of organic sulphur-containing acids has been pointed out in a number of studies[222-233]. Thus the benzhydryl ester of trichloromethanesulphenic acid rearranges to the corresponding sulphoxide on refluxing in hexane, while in polar solvents it undergoes thermal decomposition to chlorodiphenylmethane and dichlorosulphine[222]. The rearrangements of the benzhydryl esters of aromatic sulphenic[225] and sulphinic[226-228] acids to the corresponding sulphoxides and sulphones, which take place with high yields, have been described:

$$ArS{-}O{-}CH(C_6H_5)_2 \rightarrow ArS(=O){-}CH(C_6H_5)_2 ;$$

$$ArS(=O){-}O{-}CH(C_6H_5)_2 \rightarrow ArS(=O)_2{-}CH(C_6H_5)_2 .$$

A sulphone has been obtained instead of the ester on treatment of the sodium salt of toluene-*p*-sulphinic acid with benzhydryl nitrate[5].

When toluene-*p*-sulphonyl chloride is treated with diphenylmethanol, the product is dibenzhydryl ether (yield 90 to 100%) and not the expected benzhydryl ester of the sulphonic acid[223,224]. Diphenylmethane, diphenylmethanol, and benzophenone are formed on thermal decomposition of benzhydryl toluene-*p*-sulphonate[229-231]. If the latter is refluxed with benzamide in glacial acetic acid for 30 min, transbenzhydrylation takes place with formation of *N*-benzhydrylbenzamide[228]:

$$p\text{-}CH_3C_6H_4SO_3{-}CH(C_3H_5)_2 + C_6H_5CONH_2 \rightarrow C_6H_5CONH{-}CH(C_6H_5)_2 + p\text{-}CH_3C_6H_4SO_3H .$$

The reaction proceeds analogously also with propionamide[228]. The benzhydryl ester of toluene-*p*-sulphonic acid has likewise been used for the benzhydrylation of phenylacetylene[231].

2. The Bond between the Benzhydryl Group and a Sulphur Atom

The decomposition of benzhydryl sulphides with following second organic groups has been described: *N*,*N*-dimethylaminoethyl[55], benzyl[234,235], phenyl[228,236-238], benzhydryl[24,239,240], and others[235,241,242]. Di(benzhydrylthio)acetylene[243] and dibenzhydryl sulphide[244,245] have been decomposed. The oxidation of benzhydrylmethanesulphonyl sulphide by chlorine in an aqueous medium takes place in accordance with the following mechanism[246]:

$$(C_6H_5)_2CH{-}SCH_2SO_2CH_3 \xrightarrow{Cl_2} (C_6H_5)_2CHCl + ClSO_2CCl_2SO_2CH_3 .$$

When an attempt was made at the α-chlorination of benzhydryl benzyl sulphoxide by sulphuryl chloride, only the decomposition products were isolated: chlorodiphenylmethane and benzylsulphinic acid[247]. 1,1,2,2-Tetraphenylethane, dibenzhydryl ether, and debenzhydrylation products were detected among the products of the thermal decomposition of benzhydryl methyl and benzhydryl *p*-tolyl sulphoxides[233]. The following rearrangement has been described:

$$p\text{-}CH_3C_6H_4S(=O){-}CH(C_6H_5)_2 \rightleftarrows p\text{-}CH_3C_6H_4S{-}O{-}CH(C_6H_5)_2 .$$

Benzhydryl sulphides have been used to synthesise asymmetric disulphides. The *S*-benzhydryl protective group can then be removed with the aid of sulphenyl thiocyanates or thiocyanogen without affecting the disulphide bond[126,234,248,249]. Certain benzhydryl sulphides undergo very interesting reactions[126,234,248]. For example:

$$\begin{array}{c} (C_6H_5S{-}SCH_2CH_2CONHCH_2CH_2S{-})_2 \\ \uparrow S(CN)_2 \\ C_6H_5S{-}SCH_2CH_2CONHCH_2CH_2S{-}CH(C_6H_5)_2 \\ \downarrow S(CN)_2 \\ C_6H_5S{-}CH(C_6H_5)_2 \end{array} ;$$

$$(C_6H_5)_2CH{-}SCHCH_2COOH \rightarrow C_6H_5S{-}SCHCH_2COOH .$$

The thermal decomposition of benzyl diphenylmethanethiosulphonate yields a mixture of products[250]:

$$\begin{array}{c} (C_6H_5)_2CH{-}SCH_2C_6H_5 \quad SO_2 \quad (C_6H_5)_2CH{-}CH(C_6H_5)_2 \\ \uparrow \qquad\qquad \uparrow \qquad\qquad \uparrow \\ \hline \qquad\qquad\qquad | \end{array}$$

$$(C_6H_5)_2CH_2 \leftarrow (C_6H_5)_2CH{-}SO_2SCH_2C_6H_5 \rightarrow (C_6H_5)_2CS .$$

This can apparently explain the failure of the attempt to oxidise the above thiocyanate to the corresponding disulphone[251].

When di-*p*-methoxybenzhydryl *p*-tolyl sulphone is heated with ethanol in the presence of potassium hydroxide, the alcohol undergoes di-*p*-methoxybenzhydrylation with formation of the corresponding ether[15].

Benzophenone thioketals have also been subjected to decomposition[36,38,44,45,252,253].

3. The Bond between the Benzhydryl Group and a Nitrogen Atom

The decomposition of dibenzhydrylamine in the presence of alkali metal amides in liquid ammonia[254,255] and by photolysis[24,256] has been described. One of the products of the reduction of benzhydryl(benzyl)methyl amine[257,258], benzhydryl(methyl)-*p*-phenylbenzylamine[259], and other *N*-benzhydrylated compounds[260] is diphenylmethane. *sym*-Tetraphenylethane has been obtained from *N*,*N*-dibenzhydrylhydrazine[5]. The methylation of *N*-benzhydryl-*N*′,*N*′-dimethylethylenediamine by formaldehyde takes place with the removal of the benzhydryl group and the formation of the tetramethyl derivative of ethylenediamine[261]. The cleavage of benzhydrylguanidines in 80% sulphuric acid has been indicated[262]. *N*-Benzhydryl derivatives of acetamide[263], hydroxylamine[34,43,264-267], nitrosohydroxylamine[268], benzylideneamine[269], oxides[270,271], urethanes[272], *N*-substituted ammonium salts[273,274], Schiff bases[268,275-277], azo-compounds[278-283], azides[268], and other nitrogen-containing compounds[284] have also been subjected to decomposition.

An instance of the simultaneous elimination of the *O*-benzyl and *N*-benzhydryl groups is known[260].

When chlorodiphenylmethane is heated with aminoalcohols (for example with *N*,*N*-di-isopropylethanolamine), the hydrochlorides of the corresponding aminoethers are formed[285]. A mechanism has been proposed for this reaction, according to which the N atom is initially alkylated with formation of an ammonium salt; the subsequent N–O transbenzhydrylation leads to the formation of sterically hindered benzhydryl aminoethers[285]. The possibility of this mechanism has been confirmed by other studies[286,287], which showed that at 175 °C benzhydryl(β-hydroxyethyl)dimethylammonium chloride undergoes a thermal rearrangement via a similar mechanism:

$$(CH_3)_2\overset{+}{N}(Cl^-)CH_2CH_2OH \rightarrow (CH_3)_2NHCH_2CH_2O{-}CH(C_6H_5)_2 \quad .$$
$$\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad CH(C_6H_5)_2$$

The dimethylaminoalkyl ethers of diphenylmethanol are also formed on rearrangement under these conditions of other compounds of the type $[Ar_2CH\overset{+}{N}(CH_3)_2(CH_2)_nOH]Cl^-$, where $n = 2–7$. Diphenylmethanol, chlorodiphenylmethane, *sym*-tetraphenylethane, and dibenzhydryl ether have been detected as side products in this process[286,287].

There are indications in the literature of the possibility of the rearrangement of benzophenone *N*-benzyloxime to *N*-benzhydrylbenzaldoxime[34,288]:

$$(C_6H_5)_2C{=}\overset{+}{N}(O^-){-}CH_2C_6H_5 \rightarrow C_6H_5CH{=}\overset{+}{N}(O^-){-}CH(C_6H_5)_2 \quad .$$

When α,α-diaryl-*N*-benzhydrylnitrones, i.e. the *N*-benzhydryloximes of benzophenone and its derivatives, are heated to 200 °C, the corresponding isomeric *O*-benzhydryloximes are formed[34,50,264,270,271,288–298]:

$$(C_6H_5)_2C{=}\overset{+}{N}(O^-){-}CH(C_6H_5)_2 \rightarrow (C_6H_5)_2C{=}N{-}O{-}CH(C_6H_5)_2 \quad .$$

The kinetics and mechanism of this thermal rearrangement as well as the decomposition of *N*-benzhydryloximes have been widely investigated[34,264,270,271,288–297].

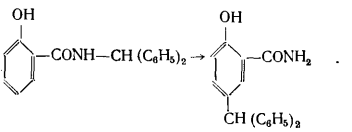
The decomposition of benzophenone Schiff bases[266,268,275,298–308], oximes[43,267,309–317], and hydrazones[139,279,318–327] has been described. The oximes have found applications in the synthesis of cycloserine (with removal of the *N*-protective group),[309–311] while the hydrazones have been used as benzhydrylating agents for carboxylic acids[319] and chlorobenzotriazole[326].

On reaction with benzylamine, the acyl derivatives of benzophenone imine give rise to the usual products of the addition of the azomethine group or are cleaved to the amides of the corresponding acids and benzophenone *N*-benzylimine[308]:

$$(C_6H_5)_2C{=}NCOR + C_6H_5CH_2NH_2 \xrightarrow{20°} [(C_6H_5)_2C(NHCH_2C_6H_5)NHCOR] \rightarrow$$
$$\rightarrow RCONH_2 + (C_6H_5)_2C{=}NCH_2C_6H_5 \quad .$$

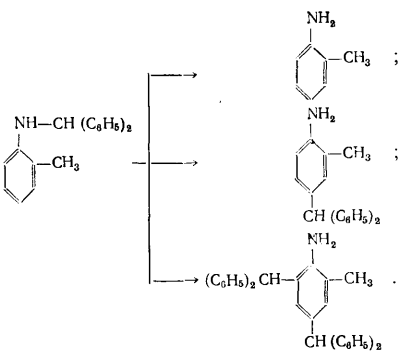
It is extremely likely that in the latter case the *N*-acylimines initially also give rise to addition products, but the latter are unstable and decompose rapidly. In one case the formation of the unstable addition products was demonstrated experimentally. In the reaction of benzylamine with benzophenone *N*-chloroacetylimine in the cold, it was possible to isolate an unstable addition product, which decomposed fully in the course of several days at a temperature as low as 20 °C.[308]

When *N*-benzhydrylsalicylamide is heated with toluene-*p*-sulphonic acid in acetic acid, the benzhydryl group migrates from the nitrogen atom to the carbon atom and 5-benzhydryl-2-hydroxybenzamide is formed[228]:



The same *N*-benzhydryl derivatives of salicylamide undergo debenzhydrylation and not hydrolysis on being refluxed for 3 h with concentrated hydrochloric acid in glacial acetic acid[328].

The lability of the bond between the benzhydryl group and the nitrogen atom in the *N*-benzhydryl derivatives of aromatic amines has been investigated[329–333]. *sym*-Tetraphenylethane was detected among the decomposition products obtained on distilling *N*-benzhydryl-*N'*,*N'*-dimethyl-*N*-phenylethylenediamine[330]. On heating to 150 °C, the hydrochloride of *N*-benzhydrylaniline gives rise to an isomerisation product (*p*-benzhydrylaniline) and also the *N*,*C*-dibenzhydryl derivative of aniline and tetraphenylethylene[331]. When *N*-benzhydryl-*o*-toluidine is heated in a mixture of acetic and hydrochloric acids, the debenzhydrylation and transbenzhydrylation reactions proceed in accordance with the following scheme[332]:

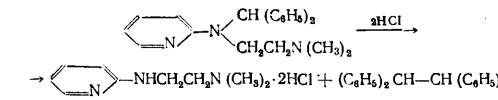


If the reaction is carried out in the presence of *o*-cresol, the *C*-benzhydrylation product of the latter is also formed[332]. It is striking that, on heating to 145 °C with hydrochloric acid, *o*-benzhydrylphenylaniline produces 1-phenylfluorene and aniline[334].

Since the alkylation of 6-azauracil takes place preferentially at the imide group, the latter must be protected in the synthesis of 6-aza-analogues of uridine and related compounds. The benzhydryl group has been used for this purpose. 1-β-D-Ribofuranosyl-6-azauracil[112], 6-azauridine 5'-phosphate[113], and their 5-methyl-derivatives have been synthesised in this way. The *N*-benzhydryl protective group has found applications in the synthesis and reactions of organophosphorus analogues of biologically active compounds[277], β-lactams[335], 1,2-dihydropyridine[336], and 9-amino-9*H*-purines[337].

The debenzhydrylation reaction takes place on hydrogenation of derivatives of *N*-benzhydrylazetidine[338–342]. Protection by the *N*-benzhydryl group has also been described for derivatives of 1,2-diazetidine and the possibilities for its removal have been investigated[343–345]. The possibility of the migration of the benzhydryl group in the benzhydryl derivatives of 2-aminopyridine has been assumed[346]. On distillation and on treatment with dry hydrogen chloride, *N*-benzhydryl-*N'*,*N'*-dimethyl-*N*-(2-pyridyl)ethylenediamine

decomposes[330]:



The same derivative of 2-aminopyridine could not be obtained by the reaction of 2-benzhydrylaminopyridine with β-chloroethyldimethylamine, since here too the debenzhydrylation reaction takes place[347]. Because of this, the attempts to synthesise 2-benzhydrylaminomethylimidazoline were also unsuccessful[261]. The hydrogenolysis of the 1-methyl- and 1-benzyl-derivatives of 4-benzhydrylpiperazine has been investigated[348]. When (pyrazinylmethyl)dimethylmethanol is refluxed in ethanol in the presence of potassium hydroxide, it undergoes reductive decomposition with formation of methylpyrazine and diphenylmethanol[349]. The hydrolysis of benzotriazolylchlorodiphenylmethane leads to the formation of benzotriazole and benzophenone, while treatment with methanol leads to benzotriazole and the dimethylacetal of benzophenone[326].

The *N*-diphenylacetyl protective group has been investigated[350–353].

III. THE BENZHYDRYL PROTECTIVE GROUP IN THE SYNTHESIS AND REACTIONS OF AMINOACIDS AND PEPTIDES

The benzhydryl and diphenylmethylene protective groups have found applications in the synthesis and study of the properties and structures of aminoacids and peptides[111,125,126,129,130,132,133,219,234,238,248,249,301,305,317,354–405]. Mention must be made of derivatives of proline[111,129,354,355], histidine[356], hydroxyaminoacids[219,357], tyrosine[357], α-vinyl-α-aminoacids[125], sulphur-containing[132,234,238,248,249,348–382] and selenium-containing[383–386] aminoacids and peptides, glucopeptides[387,388], and individual fragments of the insulin molecule[375,377–380,389].

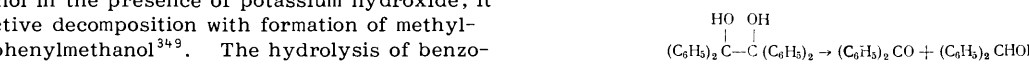
The benzhydryl group has been usually employed to protect the carboxy-group[111,126,129,130,132,133,219,383–388,390–396]. The *O*-benzhydryl[357], *N*-benzhydryl[301,356], *S*-benzhydryl[234,249,358,360,361,363–382], and *Se*-benzhydryl[384,386] protective groups have been described. We may also mention *O*-diphenylmethylene[125], *N*-benzhydryloxycarbonyl[132,359,361,362], *S*-benzhydryloxycarbonyl[132], *N*-4,4′-dimethoxybenzhydryl[364], *S*-4,4′-dimethoxybenzhydryl[364,368], *N*- and *S*-3,3′,4,4′-tetramethoxybenzhydryl[364], *N*-diphenylacetyl[353], *N*-benzhydrylacrylamide[397], *S*-α-methylbenzhydryl[369], *S*-α,4,4′-trimethylbenzhydryl[369], and other *S*-protective groups for cysteine[369]. The benzhydryl[376], 4,4′-dimethoxybenzhydryl[389,398–403], and xanthyl[404,405] groups have been used to protect the amide group in asparagine, glutamine, and in the amides of other α-aminoacids. The oxime of the *p*-polymer-substituted benzophenone has been proposed quite recently as a protective group in the synthesis of peptides[317].

One of the methods for the removal of the benzhydryl protective group is catalytic hydrogenolysis[129,130,354,355]. In the synthesis of carcinolytic peptides, the complete removal of the benzhydryl group is virtually achieved with the aid of 98% formic acid at room temperature (3 h).[392] Under mild conditions, the benzhydryl protective group can be eliminated with anhydrous hydrofluoric acid[126,376].

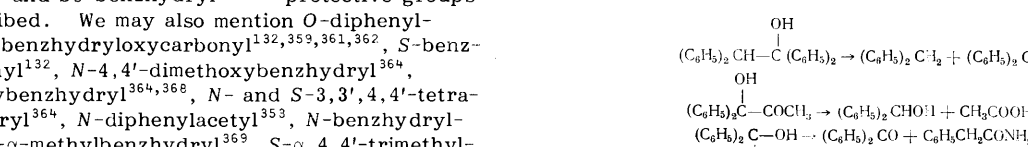
For the synthesis of asymmetric (relative to the cysteine residues) cysteine peptides, it is essential that the sulphhydryl groups should be substituted by different protective groups to permit their separate elimination[359,363]. *S*-Trityl-cysteine and *S*-benzhydrylcysteine have been proposed for this purpose. Conditions have been found for the cleavage of *S*-trityl sulphides with retention of the *S*-benzhydryl group[248,358,359,363,372–374]. The *S*-trityl protective group can be readily eliminated at room temperature by treatment with heavy metal salts. The *S*-benzhydryl group is not then affected and can be removed by treatment with trifluoroacetic acid. It has been reported[238] that *S*-trityl sulphides are cleaved by an alcoholic solution of iodine at room temperature, while their *S*-benzhydryl analogues are stable even on boiling.

IV. THE CLEAVAGE OF THE BOND BETWEEN THE BENZHYDRYL GROUP AND A CARBON ATOM

The thermal decomposition of benzopinacol was described as early as 1877:[406]



Phenyltolylpinacol behaves analogously, decomposing at the instant of fusion to phenyl tolyl ketone and phenyltolylmethanol[406]. The conversion of dinitrosotetraphenylethane into benzophenone oxime was later described[407]. Many studies devoted to the cleavage of benzopinacol[14,408–415], its derivatives and analogues[14,20,21,57,411,416,417], phenylbenzoin[39,418–421], α-*C*-substituted derivatives of diphenylmethanol[349,422–425], triphenylethanol[426–430], tetraphenylethanol[7,408,431,432], and benzhydryl phenyl ketone[429,430,432–434] were published subsequently. Less attention has been devoted to DDT,[435] 1,1-diphenylethanediol[436], benzoyldiphenylethanediol[437], benzoyltriphenylethanol[438], 1,1,2-triphenyl-1-propanol[410], 1,1,2-triphenyl-1-butanol[410], 1,1-diphenyl-4-pent-1-enol[439], 1,1,4,4-tetraphenylbuta-1,2-dien-4-ol [40] and its 3-substituted derivatives[441], hexaphenylallene glycol[440], benzhydryl methyl ketone[279], benzhydryl benzyl ketone[442], *p*-anisyl benzhydryl ketone[429], dibenzhydryl ketone[30], benzhydryl α-hydroxybenzhydryl ketone[30], benzoyldiphenylaminomethane[39], 1,2,2-triphenylaminomethane[428], triphenylaminoethanol[254], triphenylacetamide[443], 2-diphenylacetyl-1-methylbenzimidazole[444], and other *S*-benzhydrylated compounds[39,84,85,417,425,445–449]. The products of the cleavage of the above compounds are as a rule diphenylmethane, diphenylmethanol, and diphenyl ketone:



In an early investigation Chichibabin showed[450,451] that pentaphenylethane decomposes at an elevated temperature at the C–C bond of ethane, like hexaphenylethane. In this case the pentaphenylethane molecule decomposes into radicals, which then recombine differently:

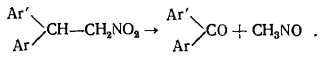


According to the observations of Cone and Robinson[452], treatment of this compound with phosphorus pentachloride yields chlorotriphenylmethane. The instability of the central C–C bond in pentaphenylethane was subsequently investigated by other workers[12,453–461]. The dissociation of the carbon–carbon bond in *sym*-tetraphenylethane[12,455,462–464] and *p*-benzhydrylphenyltriphenylmethane[36,465] was indicated.

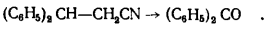
The photolysis of 1,1,2,2-tetraphenylethane, 1,1,3,3-tetraphenylpropane, 1,1,4,4-tetraphenylbutane, and 1,1,5,5-tetraphenylpentane has been described[24,466,467]. The oxidation of 1,1-diphenylethane, 1,1-diphenylpropane,

1,1-diphenylbutane, 1,1-diphenylpentane, and 1,1,diphenylhexane by oxygen has been investigated[468,469]. It has been shown that tertiary carbon atoms are acted upon by oxygen with formation of hydroperoxides, whose decomposition leads to the formation of benzophenone, its oxidation products, and tarry substances. The product of the electrochemical oxidation of diphenylacetic acid in water is diphenylmethanol, while the same reaction in acetonitrile gives rise to a mixture of diphenylmethane, tetraphenylethane, and the benzhydryl ether of the starting material[470,471].

Attention has been drawn[472] to the anomalous course of the Nef reaction with salts of 1,1-diaryl-2-nitroethanes, in which diaryl ketones are obtained instead of the corresponding diarylacetaldehydes:

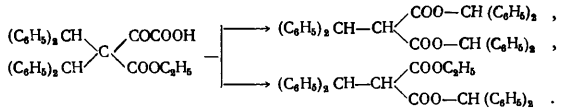


The oxidative hydrolysis of 3,3-diphenylpropionitrile, one of the products of which is diphenyl ketone (yield 22%), has been described quite recently[473]:



Diphenylmethane (yield 49%) and 1,1,2,2-tetraphenylmethane (yield 6%) have been detected and isolated from the products of the thermolysis (250 °C, NaH) of 1,1-diphenylpropanone azine $[(C_6H_5)_2CHC(CH_3)=N-]_2$.[474] The formation of the expected pyrrole derivatives is not observed under these conditions.

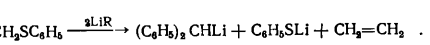
When β,β-dibenzhydryl-β-ethoxycarbonyl-α-oxopropionic acid is heated for 20 min at 190–200 °C, the following benzhydryl derivatives of malonic acid are formed[475]:



It has been found[476] that the reaction of trichloroethylene and 2-chloro-1,1-diphenylethylene with benzene in the presence of aluminium chloride results in the formation of polynuclear condensation products, which give rise to anthracene, triphenylmethane, and diphenylmethane on thermal decomposition. These experiments were subsequently repeated[463].

2-Hydroxy-1,4-naphthoquinone and benzophenone are formed in the oxidation and other reactions of 2-benzhydryl-1,4-naphthoquinone[477]. The interaction of 2,3-dibenzhydryl-1-phenylnaphthalene with benzene in the presence of aluminium chloride gives rise to triphenylmethane, 1-phenylnaphthalene, and its isomerisation product—2-phenylnaphthalene[478].

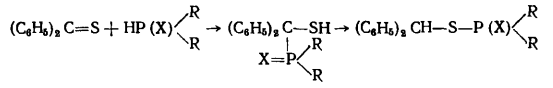
The reaction of 3,3-diphenylpropyl phenyl sulphide under the influence of an organolithium compound proceeds in accordance with the following mechanism[479]:



If the SC_6H_5 group is replaced by the $NHSO_2C_6H_5$ group, the oxidation of the resulting compound with potassium permanganate gives rise to benzophenone[480].

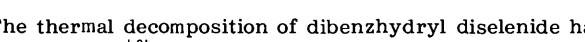
V. THE CLEAVAGE OF THE BONDS BETWEEN THE BENZHYDRYL GROUP AND OTHER ATOMS

It has been shown[481] that dibutylphosphinous and dibutylphosphonothious acids react with thiobenzophenone in the absence of catalysts at room temperature. The main products isolated in all cases were the isomeric *S*-benzhydryl phosphorothioates and their analogues instead of the expected α-mercapto-derivatives of phosphorus acids:

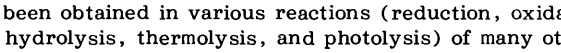


Such isomerisation of α-mercapto-derivatives of phosphorus acids, i.e. the C → S migration of the phosphoryl and thiophosphoryl groups, has been investigated also in relation to other examples[481]. α-Mercapto benzhydrylphosphonites rearrange on heating to benzhydrylphosphonothionates[482].

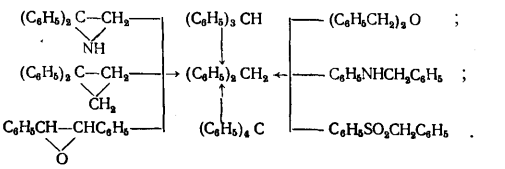
Benzhydryl acetate has also been obtained in accordance with the following mechanism[483]:



The thermal decomposition of dibenzhydryl diselenide has been described[484]:



Diphenylmethane, diphenylmethanol, and diphenyl ketone have been obtained in various reactions (reduction, oxidation, hydrolysis, thermolysis, and photolysis) of many other compounds containing phenyl groups (usually attached to a carbon atom), for example:



These instances of the formation of the benzhydryl group are not considered in this review, since they can be only formally included among debenzhydrylation reactions.

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